Supporting Information

for the manuscript entitled

Sulfamate Esters Guide C(3)-Selective Xanthylation of Alkanes

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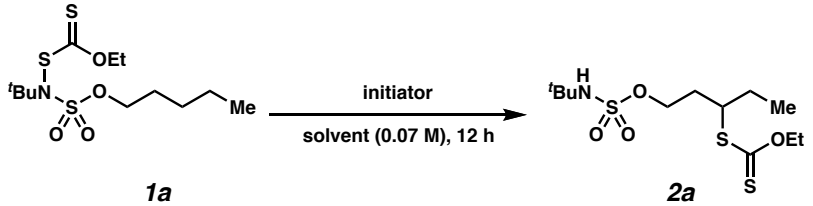
I. pK_a Calculations.

To predict p*K*a values for a sulfamates **1a–e**, SPARC[1] has been used. SPARC has been developed using a training set of empirically derived ionization constants (aqueous p*K*a values) to derive linear free-energy relationships, which are the basis for p*K*a predictions. For the purpose of these calculations, the calculation type is "p*K*a", the sub-calculation type is "full speciation". "Full speciation" provides macroscopic p*K*a values based on the number of ionizable sites (N). Specifically, macroconstants are based on $N*2^{(N-1)}$ microconstants. Calculations assume a temperature of 25 °C, and do not consider tautomers or hydration state.

II. Optimization of C–H Xanthylation.

General procedure.
In a flame-dried microwave vial equipped with magnetic stir bar and sealed with a crimp cap, pentyl *tert*-butyl *N*-xanthylsulfamate (96 mg, 0.28 mmol, 1.0 equiv) and initiator (10 mol%) was dissolved in anhydrous solvent (4.0 mL, 0.07 M) under an inert atmosphere. The vial was then stirred at specified temperature (see table **S1**) for 12 h. After the allotted time, the crude reaction reaction mixture was concentrated *in vacuo* The resulting crude material was purified by flash column chromatography on silica gel column, eluting with a hexanes:EtOAc (90:10) solvent system.

Table S1. Optimization of reaction conditions[a]



1a ***2a***

entry	Initiator	T °C	Solvent	***1a*** (%)[b]	***2a*** (%)[b]
1[c]	**26 W CFL**	**35 – 38**	CH_3CN	**–**	**91**
2	AIBN	80	PhH	36	24
3	DLP	80	PhH	–	61
4	BPO	80	PhH	–	53
5	(^{t}BuO)$_2$	120	PhCl	–	36
6[d]	–	21		≥ 95	–
7[d]	–	50		≥ 95	–

[a]General reaction conditions: reactions performed on 0.28 mmol scale with 1.0 equiv ***1a***, 4.0 mL of solvent under nitrogen atmosphere, 12 h. [b]Isolated yield. [c]vial was then placed in front of the light source (ca. 3 cm from source) and irradiated. [d]Reaction shielded from ambient light.
AIBN = azobissisobutyronitrile, DLP = dilauroyl peroxide, BPO = benzoyl peroxide

[1] a) Hilal, S. H.; Karickhoff, S. W. A Rigorous Test for SPARC's Chemical Reactivity Models: Estimation of More Than 4300 Ionization pK$_a$s. *Quant. Struct.-Act. Relat.* **1995**, *14*, 348.
(b) http://www.archemcalc.com/sparc.html.

III. Description of Quantum Yield Experiments.

Determination of Light Intensity.
The procedure of Yoon and co-workers[2] was followed to determine the photon flux of the spectrophotometer. All solutions were stored in the dark when not in use. Manipulations were performed with the lights off and care was taken such that samples were protected from ambient light as much as possible.

Preparation of stock solutions.
A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate trihydrate ($[K_3Fe^{III}(C_2O_4)_3]\bullet 3H_2O$; 1.84 g, 3.75 mmol) in 0.05 M H_2SO_4 (25 mL total volume).

A buffered phenanthroline solution was prepared by dissolving phenanthroline (50 mg, 0.277 mmol) and sodium acetate (11.25 g) in 0.5M H_2SO_4 (50 mL total volume).

Determination of background Fe^{2+} concentration.
2.00 mL of the ferrioxalate solution was added to a quartz cuvette. Next 0.35 mL of the phenanthroline solution was added and the mixture was stored in the dark for 1 hour. Then the UV-Vis spectrum was obtained. The absorbance value at 510 nm was recorded. This process was repeated an additional 2 times.
Trial 1: 0.3361698985
Trial 2: 0.3350063562
Trial 3: 0.3769177198
Average value: 0.349364658

Determination of photon flux.
2.00 mL of the ferrioxalate solution was added to a quartz cuvette. The cuvette was immediately irradiated with ultraviolet light (313 nm +/– 5 nm) in a spectrophotometer for 90 seconds. The cuvette was then removed from the spectrophotometer, 0.35 mL of the phenanthroline solution was added to the ferrioxalate solution, and the resulting mixture was stored in the dark for 1 hour. Then the UV-Vis spectrum was then obtained. The absorbance value at 510 nm was recorded. This process was repeated an additional 2 times.
Trial 1: 1.48140192
Trial 2: 1.35229826
Trial 3: 1.48975372
Average value: 1.4411513

Calculations.
The amount of Fe^{2+} formed was calculated according to the following equation:

$$mol\ Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon}$$

[2] Cismesia, M. A.; Yoon, T. P. Characterizing chain processes in visible light photoredox catalysis. *Chem. Sci.* **2015**, *6*, 5426–5434.

where V is the volume of the sample analyzed (2.35 mL), ΔA is the difference in average absorbances (between irradiated and unirradiated ferrioxalate solutions) at 510 nm, l is the path length, and ε is the molar absorptivity at 510 nm.

$$mol\ Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} = \frac{(0.00235\ L) \cdot (1.091786642)}{(1.00\ cm) \cdot \left(11{,}100\ {}^{L}/_{mol \cdot cm}\right)} = 2.31144 \cdot 10^{-7}\ mol$$

The fraction of light absorbed by the ferrioxalate actinometer was calculated by the following equation:

$$f = 1 - 10^{-A}$$

where A is the absorbance at 313 nm of the ferrioxalate actinometer solution prior to irradiation and addition of phenanthroline.

$$f = 1 - 10^{-A} = 1 - 10^{-4.54854202} = 0.999971721 \approx 1.000$$

The photon flux was calculated using the following equation:

$$photo\ flux = \frac{mol\ Fe^{2+}}{\phi \cdot t \cdot f}$$

where ϕ is the quantum yield of for the ferrioxalate actinometer at 313 nm,[3] t is the time and f is the fraction of light absorbed by the ferrioxalate actinometer solution.

$$flux = \frac{mol\ Fe^{2+}}{\phi \cdot t \cdot f} = \frac{2.31144 \cdot 10^{-7}\ mol}{(1.24\ einstein^{-1}) \cdot (90\ s) \cdot (1.000)} = 2.07118 \cdot 10^{-9}\ {}^{einstein}/_{s}$$

Determination of quantum yield.

In a nitrogen-filled glovebox, a quartz cuvette was charged with pentyl *tert*-butyl((ethoxycarbonothioyl)thio) sulfamate ester (60.2 mg, 0.175 mmol, 1.0 equiv). MeCN (2.5 mL, 0.07 M) was added and the vial was fitted with a Teflon cap and sealed with parafilm. The vial was then placed in the spectrophotometer and irradiated with ultraviolet light (313 nm, +/– 5 nm) for 4 hours. After 4 hours, the vial was removed from the spectrophotometer and the reaction mixture was transferred to a scintillation vial. The cuvette was rinsed with CH_2Cl_2 (2 x 3 mL) to achieve quantitative transfer. The solvent was then removed under reduced pressure and the resulting residue was purified as detailed above to provide the desired product (30.2 mg, 50% yield, 0.0879 mmol).

The procedure was repeated one more time to yield the desired product (31.3 mg, 52% yield, 0.0911 mmol).

[3] Hatchard, C. G.; Parker, C. A. A new sensitive chemical actinometer – II. Potassium ferrioxalate as a standard chemical actinometer. *Proc. R. Soc. London Ser. A* **1956**, *235*, 518–536.

The minimum quantum yield (ϕ) was calculated using the following equation:

$$\phi = \frac{mol\ product}{flux \bullet t \bullet f}$$

where t is the reaction time and f is the fraction of light absorbed by pentyl chloro(*tert*-butyl)sulfamate.

Trial 1:

$$\phi = \frac{mol\ product}{flux \cdot t \cdot f} = \frac{0.0000879\ mol}{(2.07118 \cdot 10^{-9} einstein \cdot s^{-1}) \cdot (14400\ s) \cdot (1.000)} = 2.95\ \approx 3.000$$

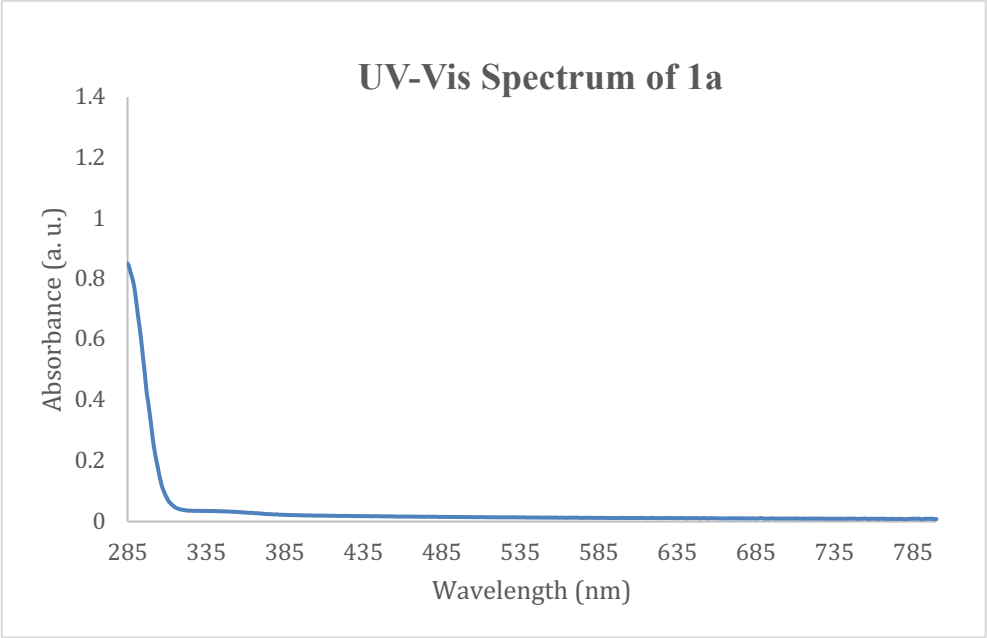
Trial 2:

$$\phi = \frac{mol\ product}{flux \cdot t \cdot f} = \frac{0.0000911\ mol}{(2.07118 \cdot 10^{-9} einstein \cdot s^{-1}) \cdot (14400\ s) \cdot (1.000)} = 3.05\ \approx 3.000$$

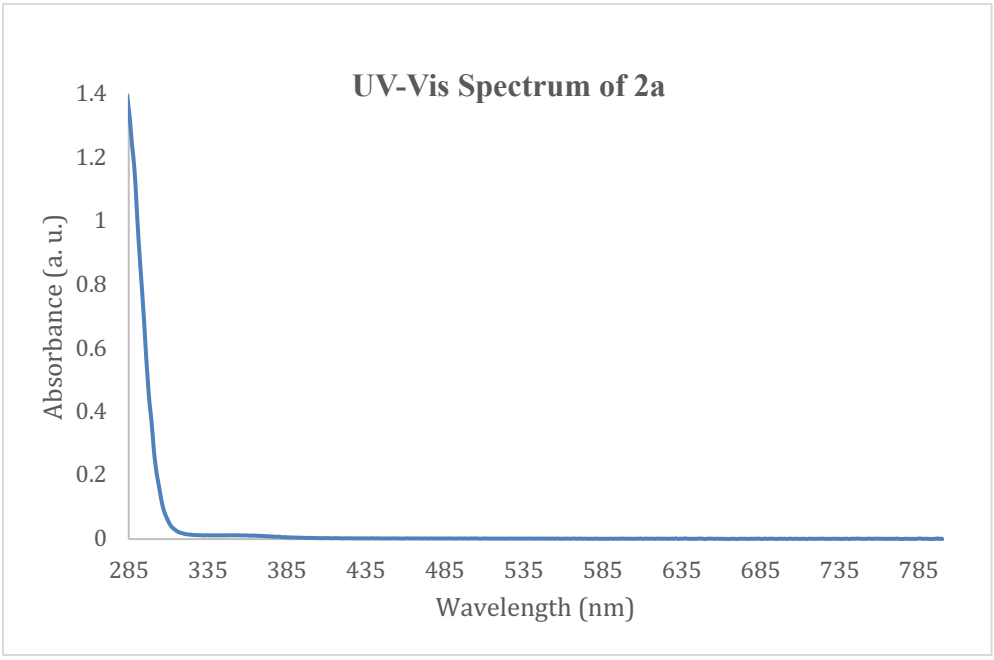
$$Average\ \phi = 3.00$$

IV. UV-Vis Spectra.

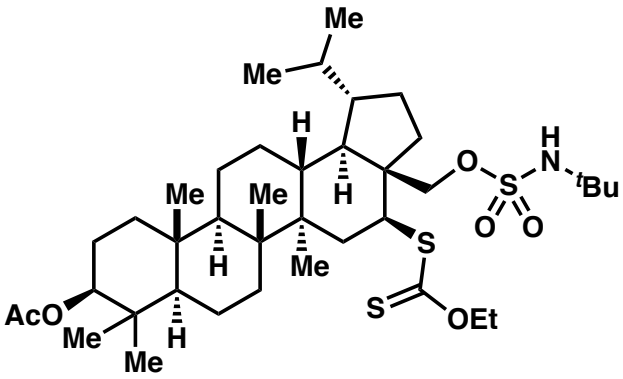
Pentyl *tert*-butyl((ethoxycarbonothioyl)thio)sulfamate (**1a**) in MeCN.

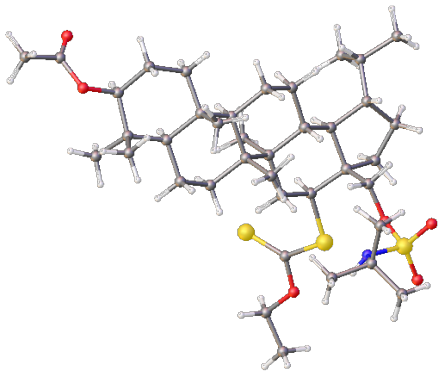


3-((ethoxycarbonothioyl)thio)pentyl *tert*-butylsulfamate (**2a**) in MeCN.



V. Crystallographic Analyses.





Crystal structure report of betulin-derived **2q**. ORTEP diagram (on the right) showing thermal ellipsoids at the 50% probability level.

A specimen of $C_{41}H_{69}Cl_6NO_6S_3$, approximate dimensions 0.217 mm x 0.227 mm x 0.326 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker-Nonius X8 Kappa APEX II system equipped with a fine-focus sealed tube (MoKα, λ = 0.71073 Å) and a graphite monochromator. The total exposure time was 12.69 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombicunit cell yielded a total of 62494 reflections to a maximum θ angle of 28.28° (0.75 Å resolution), of which 12089 were independent (average redundancy 5.169, completeness = 99.9%, R_{int} = 5.66%, R_{sig} = 5.40%) and 10470 (86.61%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.2495(5) Å, b = 15.2792(8) Å, c = 34.4997(17) Å, volume = 4875.7(4) $Å^3$, are based upon the refinement of the XYZ-centroids of 9512 reflections above 20 σ(I) with 4.559° < 2θ < 56.64°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.929. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8480 and 0.8950. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with Z = 4 for the formula unit, $C_{41}H_{69}Cl_6NO_6S_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 540 variables converged at R1 = 7.82%, for the observed data and wR2 = 22.52% for all data. The goodness-of-fit was 1.145. The largest peak in the final difference electron density synthesis was 0.836 $e^-/Å^3$ and the largest hole was -1.117 $e^-/Å^3$ with an RMS deviation of 0.125 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.336 g/cm^3 and F(000), 2080 e^-.

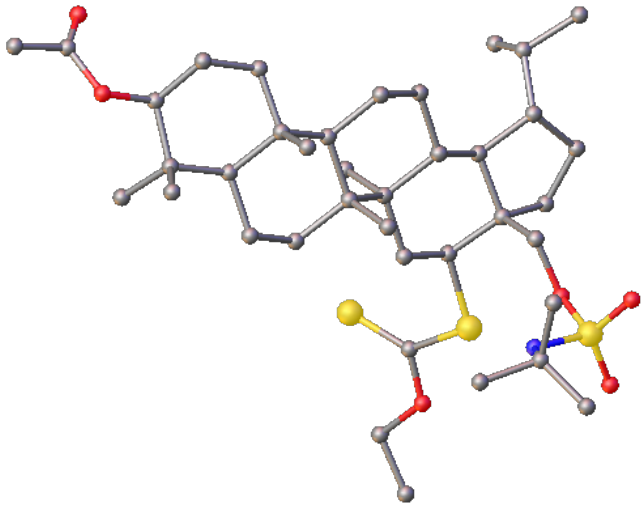
Crystal data and structure refinement for betulin-derived **2q**

Identification code rds804

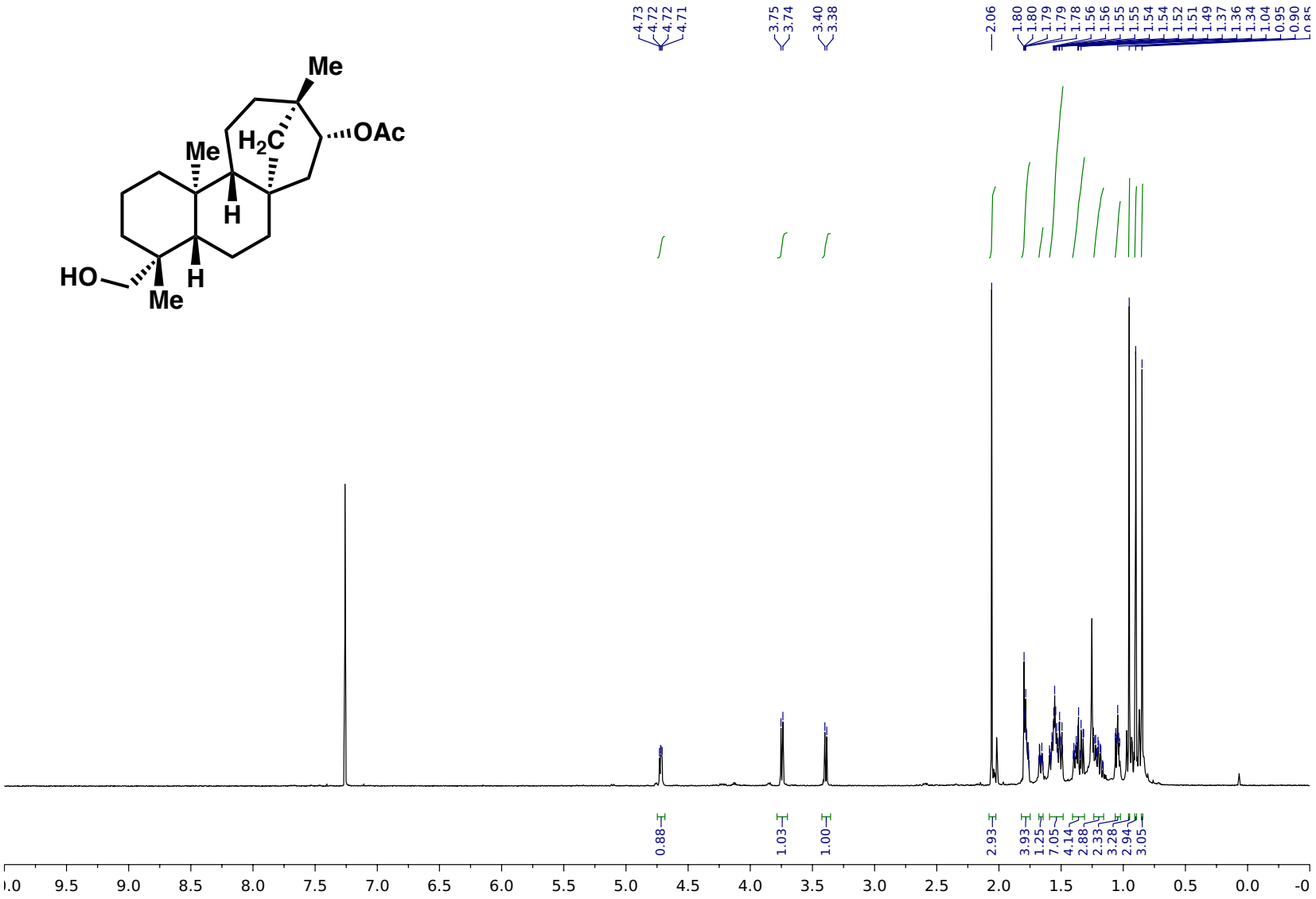
Chemical formula	$C_{41}H_{69}Cl_6NO_6S_3$
Formula weight	980.85 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.217 x 0.227 x 0.326 mm
Crystal system	orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 9.2495(5) Å α = 90° b = 15.2792(8) Å β = 90° c = 34.4997(17) Å γ = 90°
Volume	4875.7(4) $Å^3$
Z	4
Density (calculated)	1.336 g/cm^3
Absorption coefficient	0.524 mm^{-1}
F(000)	2080
Diffractometer	Bruker-Nonius X8 Kappa APEX II
Radiation source	fine-focus sealed tube (MoKα, λ = 0.71073 Å)
Theta range for data collection	1.78 to 28.28°
Index ranges	-12<=h<=12, -20<=k<=19, -45<=l<=45
Reflections collected	62494
Independent reflections	12089 [R(int) = 0.0566]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8950 and 0.8480
Structure solution technique	direct methods
Structure solution program	XS, VERSION 2013/1
Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)
Function minimized	Σ w(Fo2 - Fc2)2
Data / restraints / parameters	12089 / 42 / 540
Goodness-of-fit on F2	1.145
Final R indices	10470 data; I>2σ(I) R1 = 0.0782, wR2 = 0.2179

	all data R1 = 0.0903, wR2 = 0.2252
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1090P)^2+10.5661P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.11(12)
Largest diff. peak and hole	0.836 and -1.117 eÅ^{-3}
R.M.S. deviation from mean	0.125 eÅ^{-3}

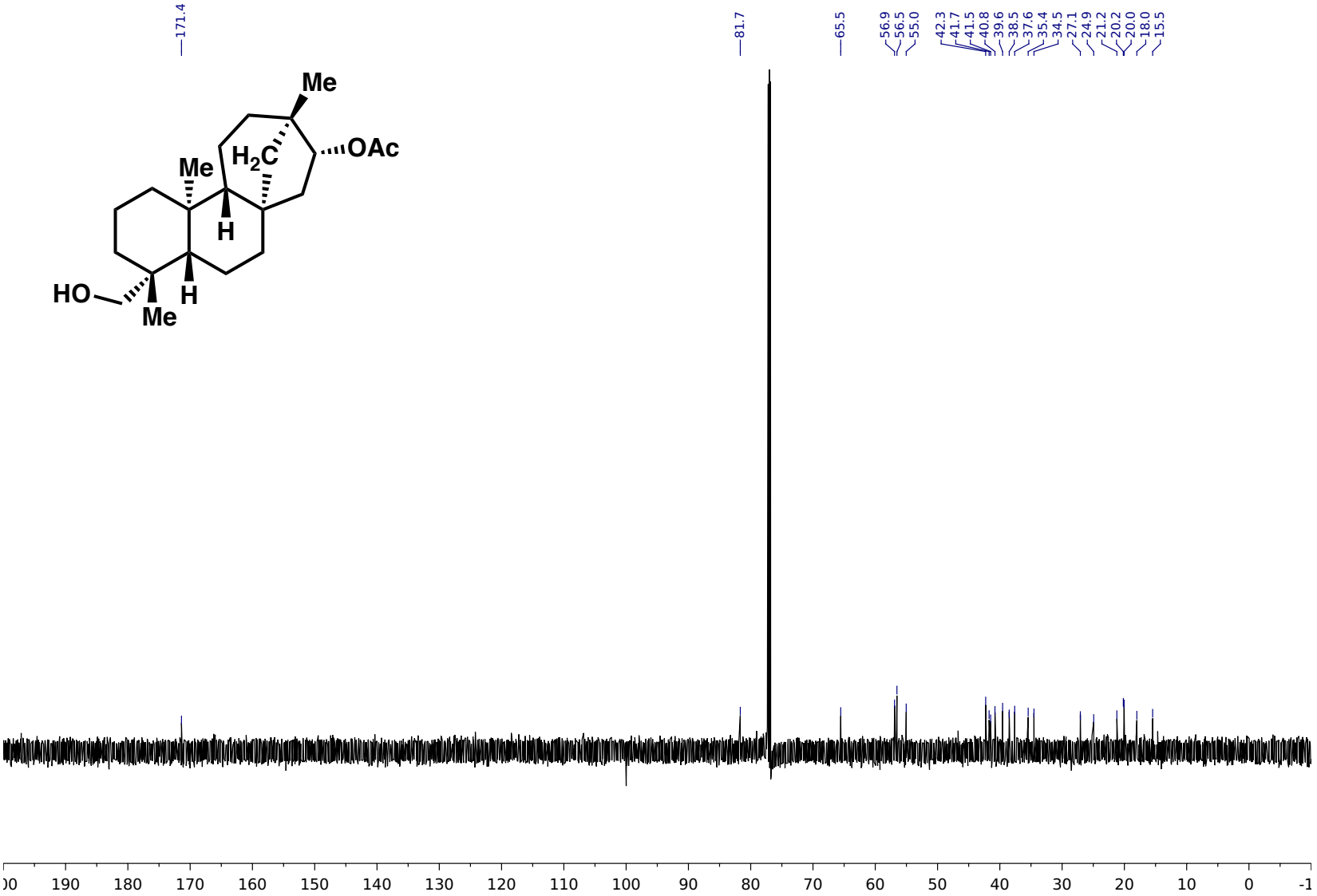
CCDC #1860160 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures



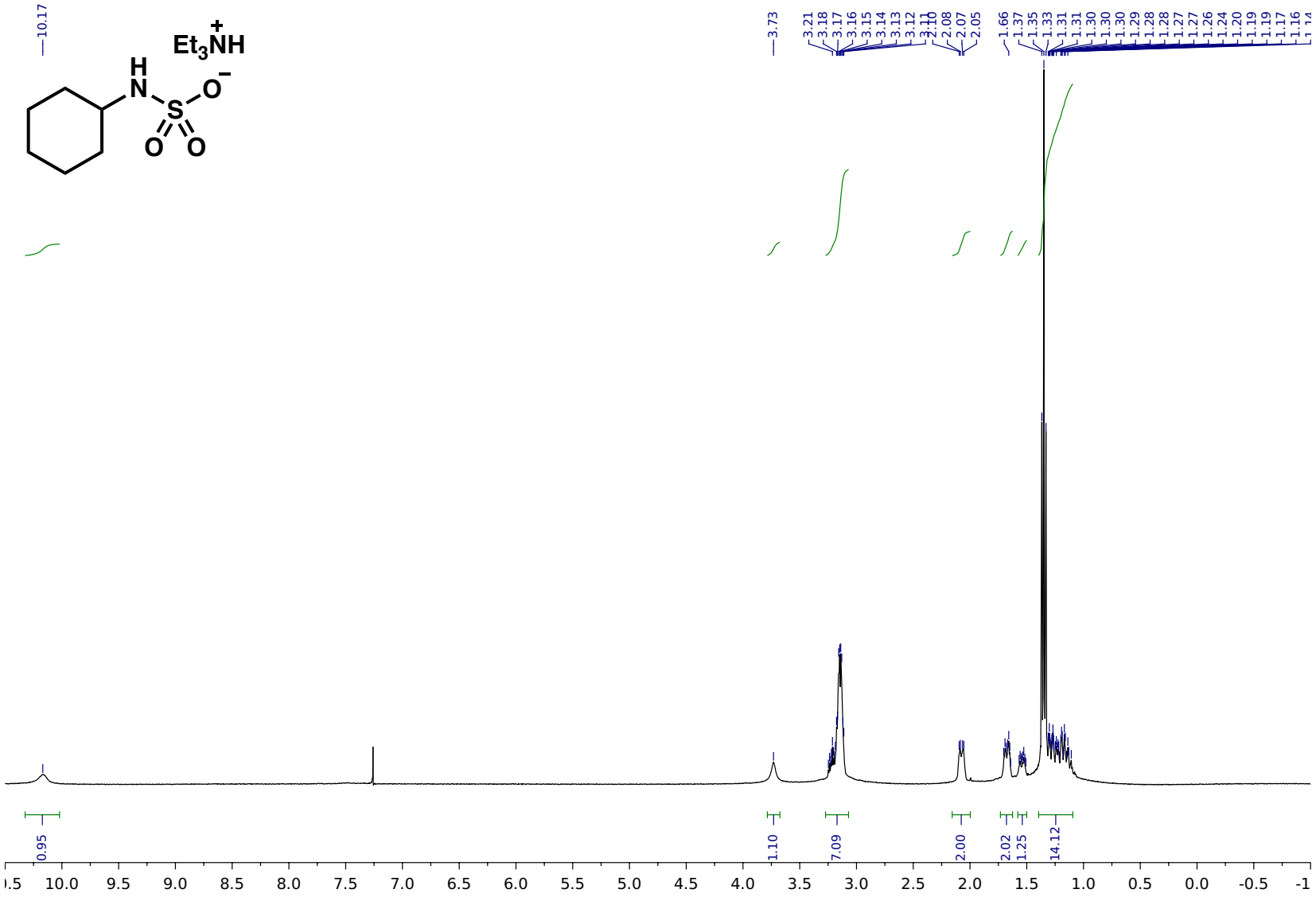
ORTEP diagram of major diastereomer of **2q** showing thermal ellipsoids at the 50% probability level.



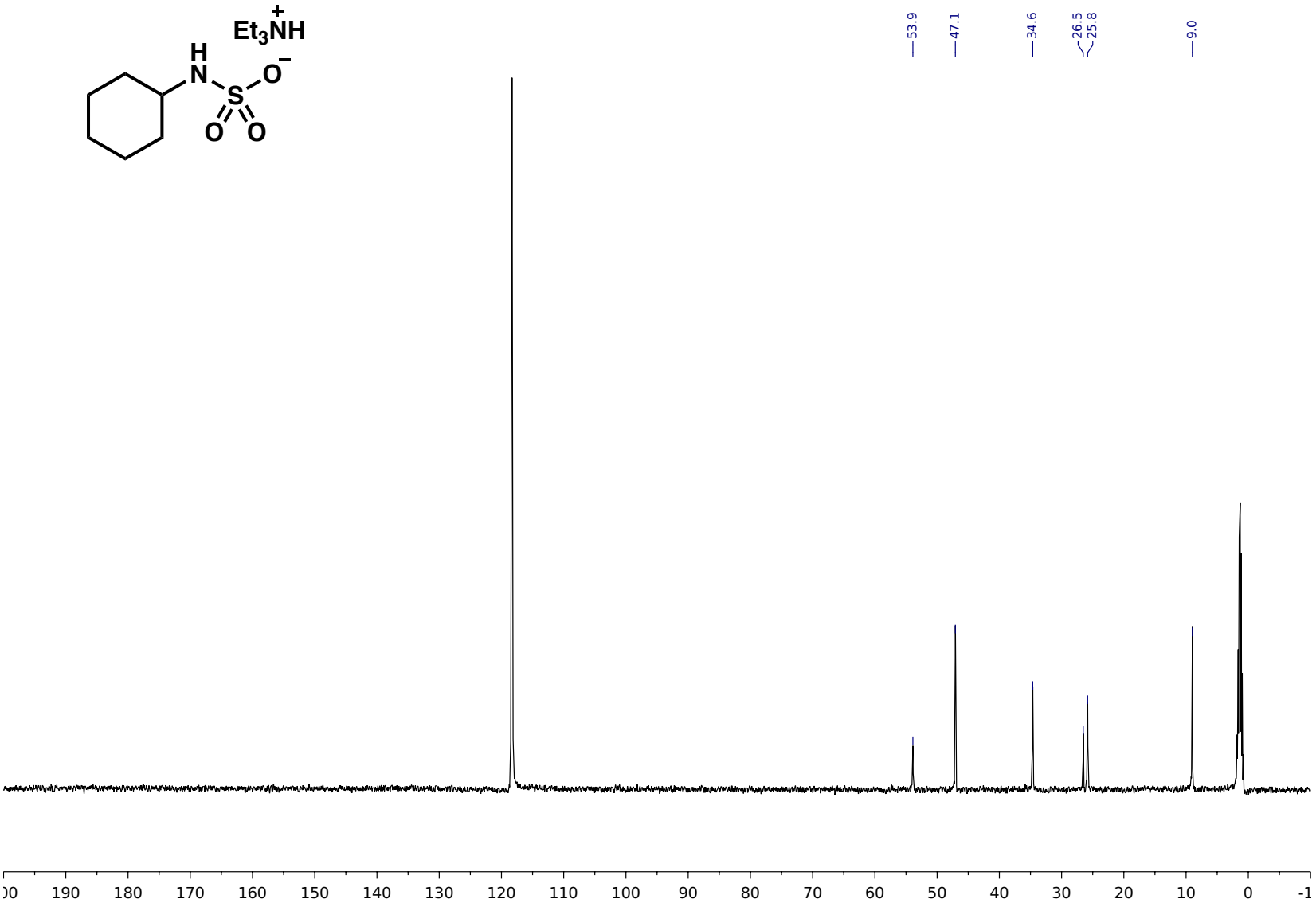
^{1}H NMR (700 MHz, $CDCl_3$) for (–)-16-acetoyxy-18-hydroxy-13-methyl-17-norkaurane (**S2**)



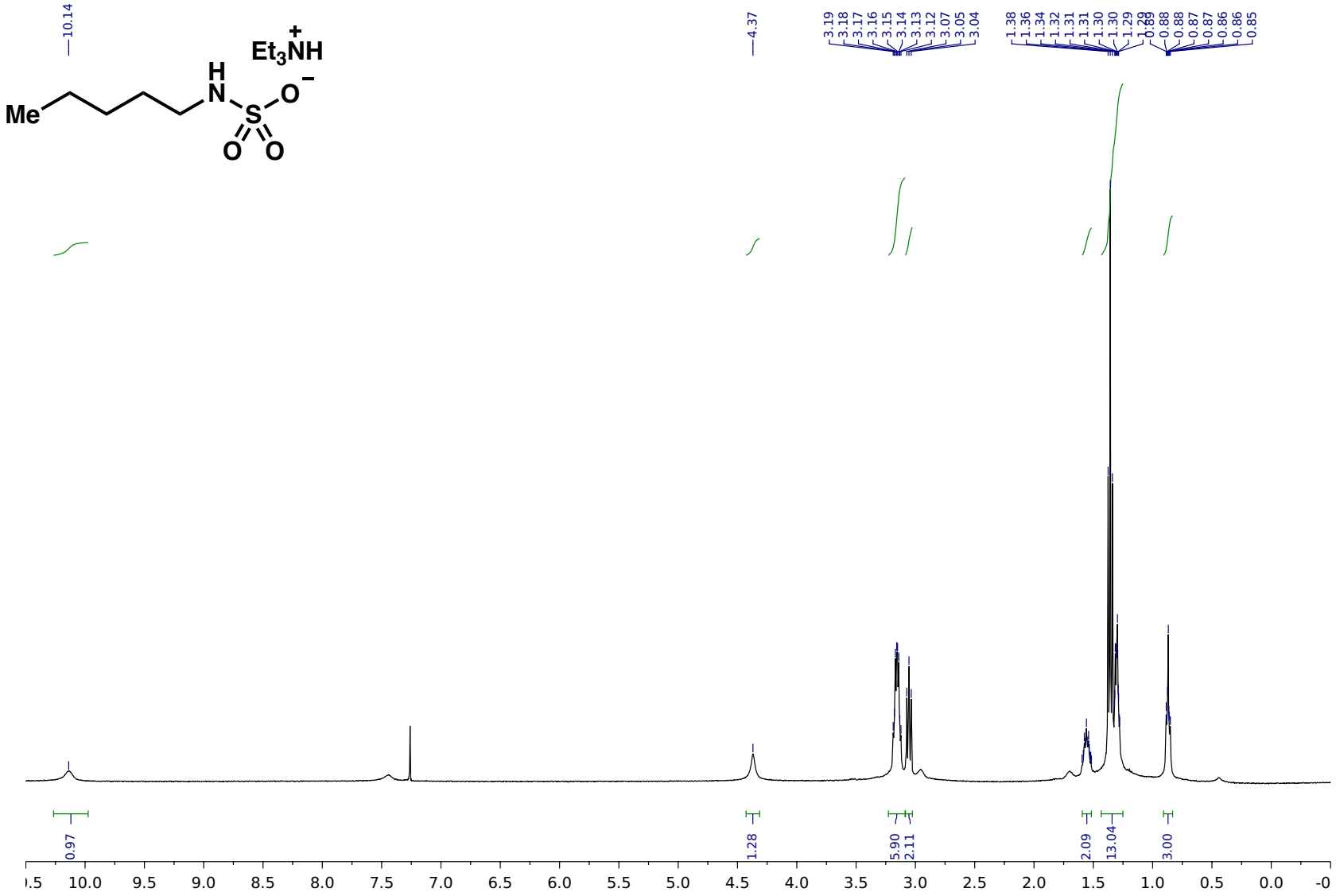
$^{13}C\{1H\}$ NMR (176 MHz, $CDCl_3$) for (–)-16-acetoyxy-18-hydroxy-13-methyl-17-norkaurane **(S2)**



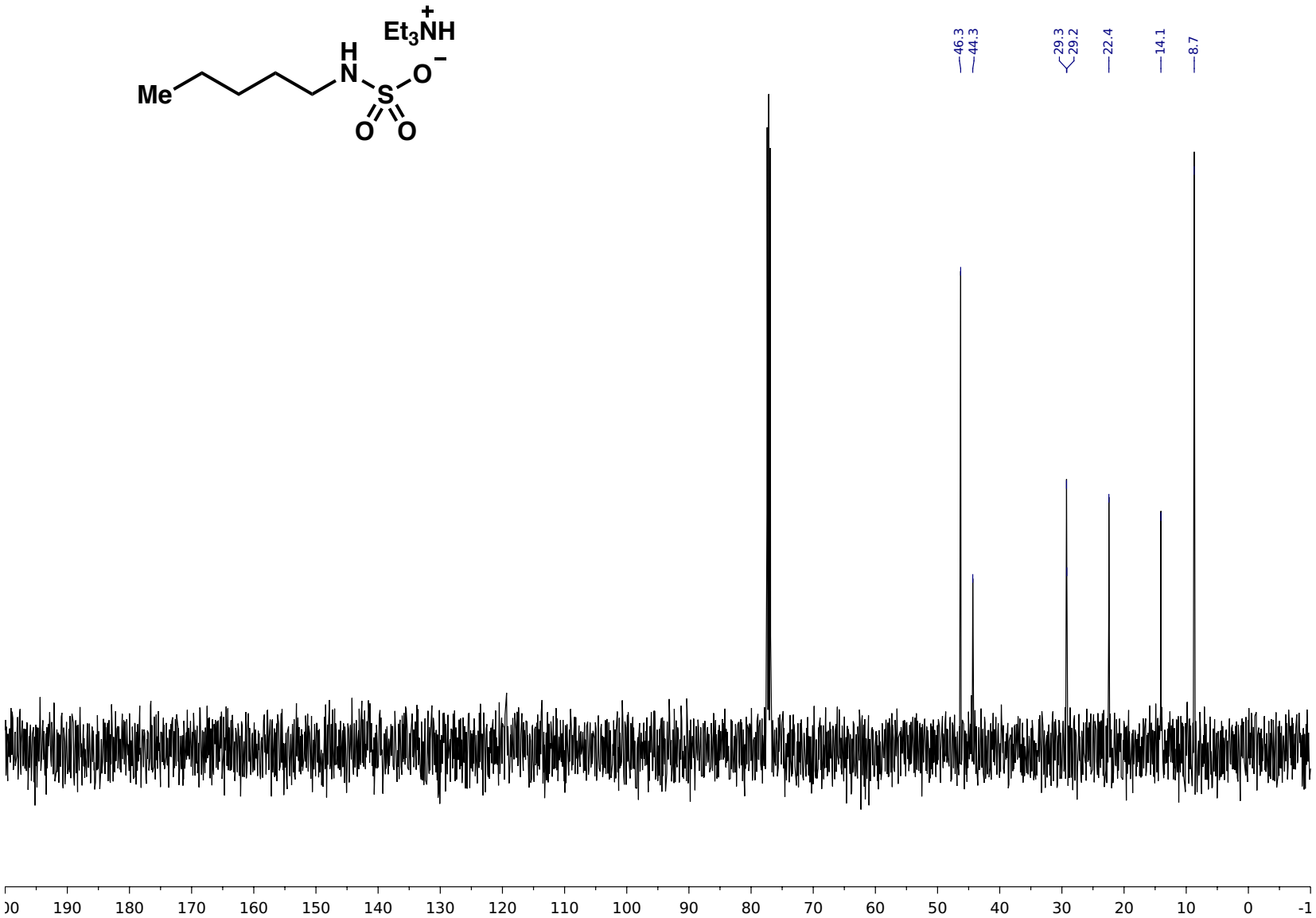
^{1}H NMR (400 MHz, $CDCl_3$) for triethylammonium cyclohexylsulfamate (**S3f**)



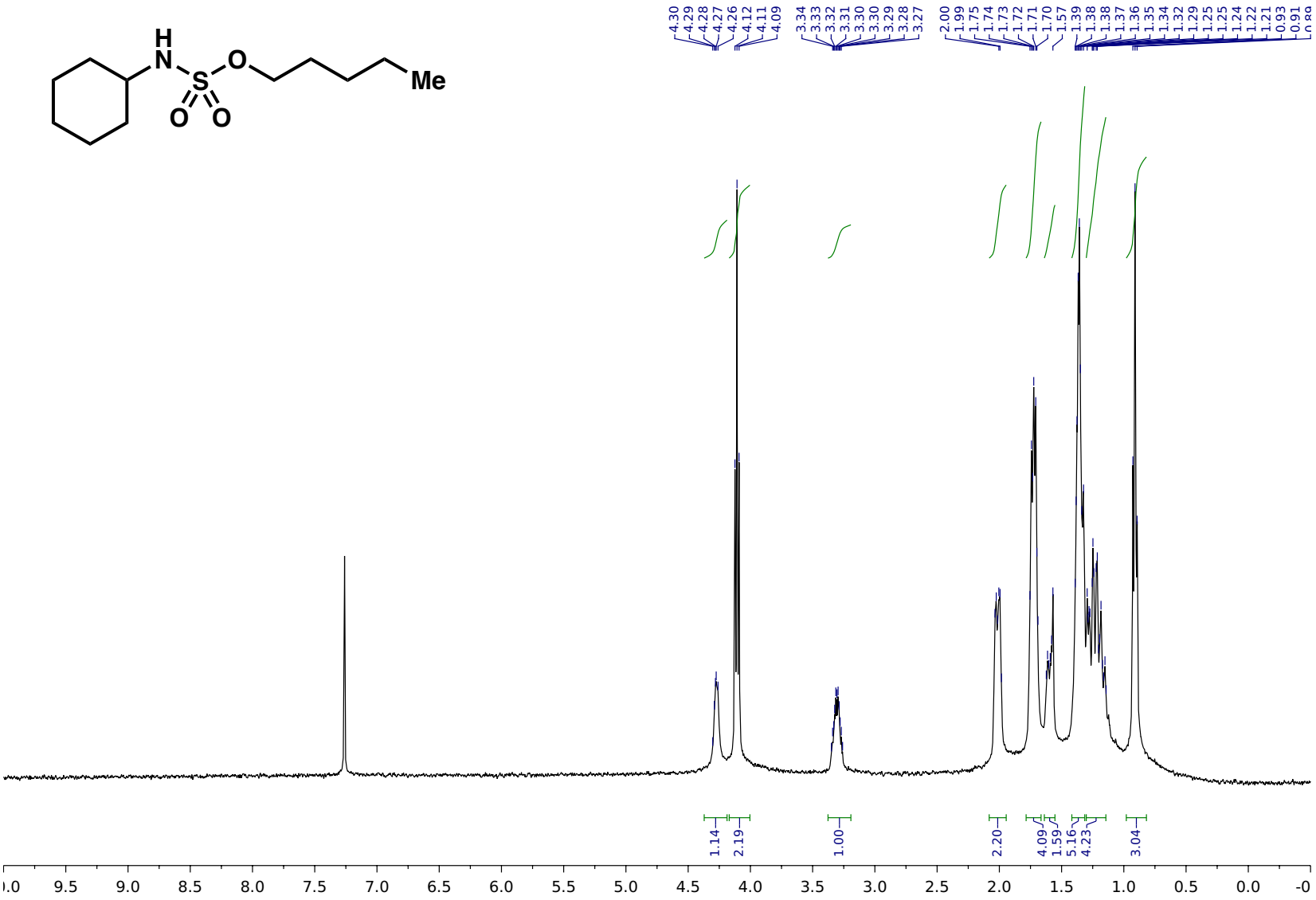
$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3CN) for triethylammonium cyclohexylsulfamate (**S3f**)



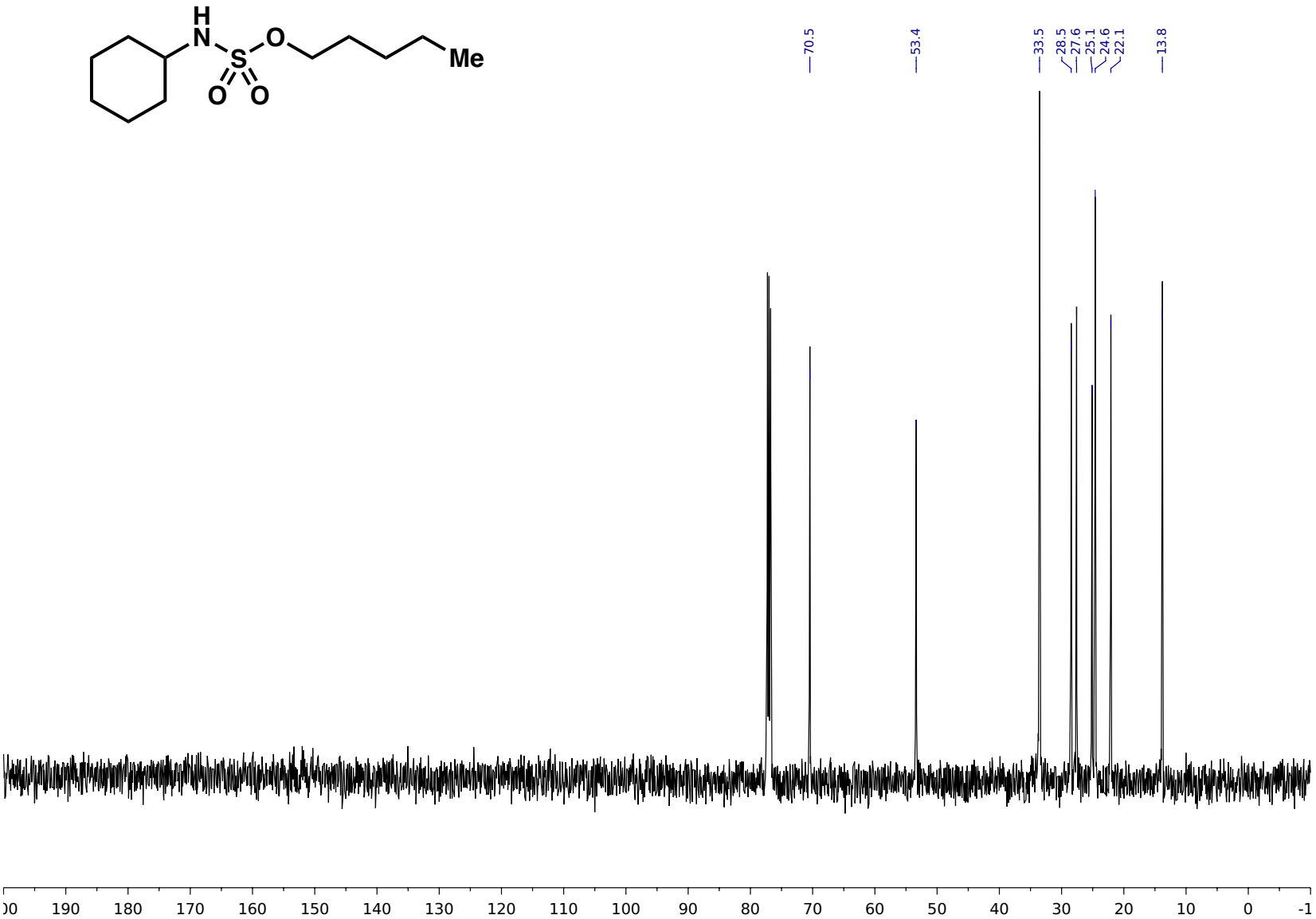
^{1}H NMR (400 MHz, $CDCl_3$) for triethylammonium pentylsulfamate (**S3g**)



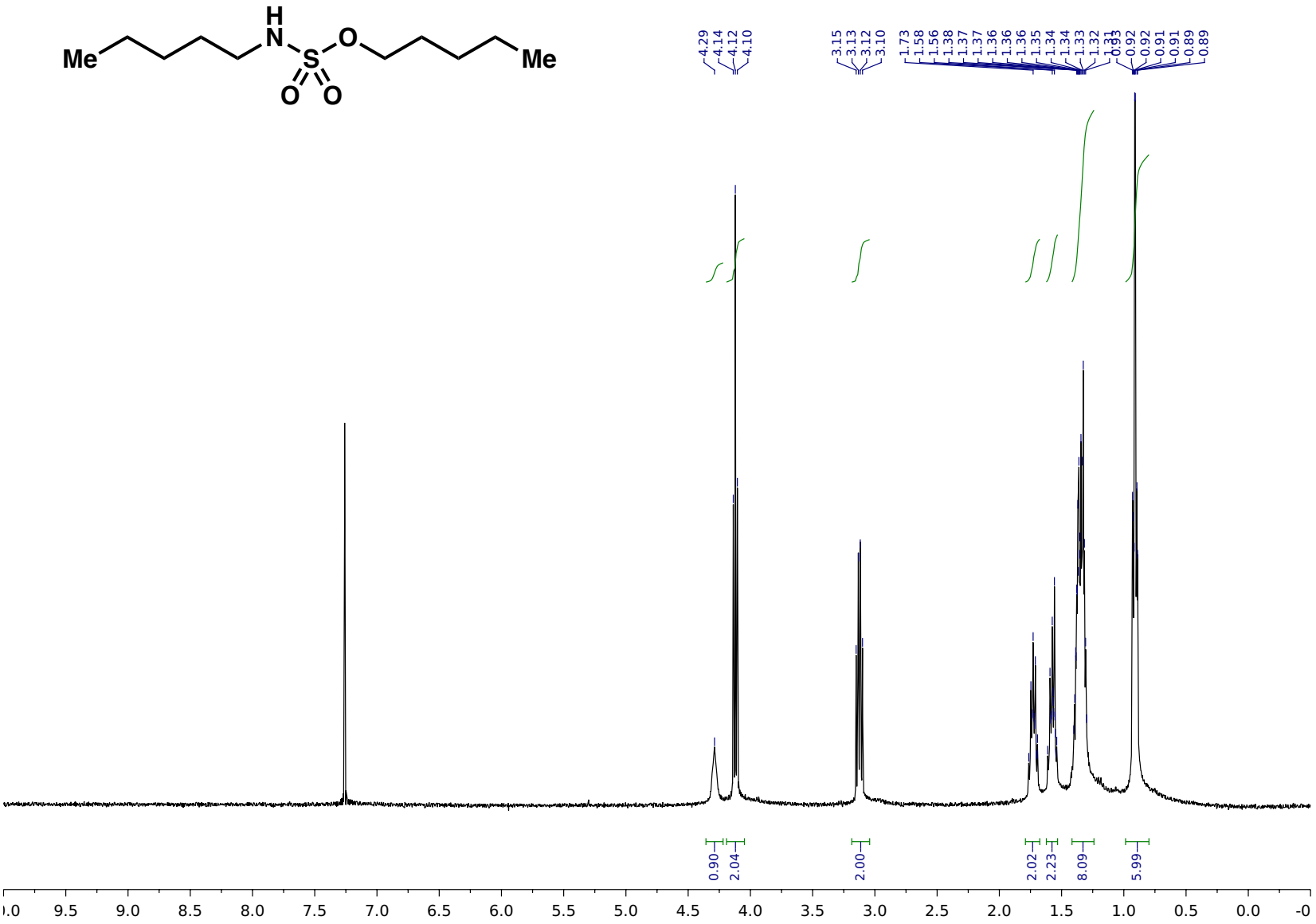
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for triethylammonium pentylsulfamate (**S3g**)



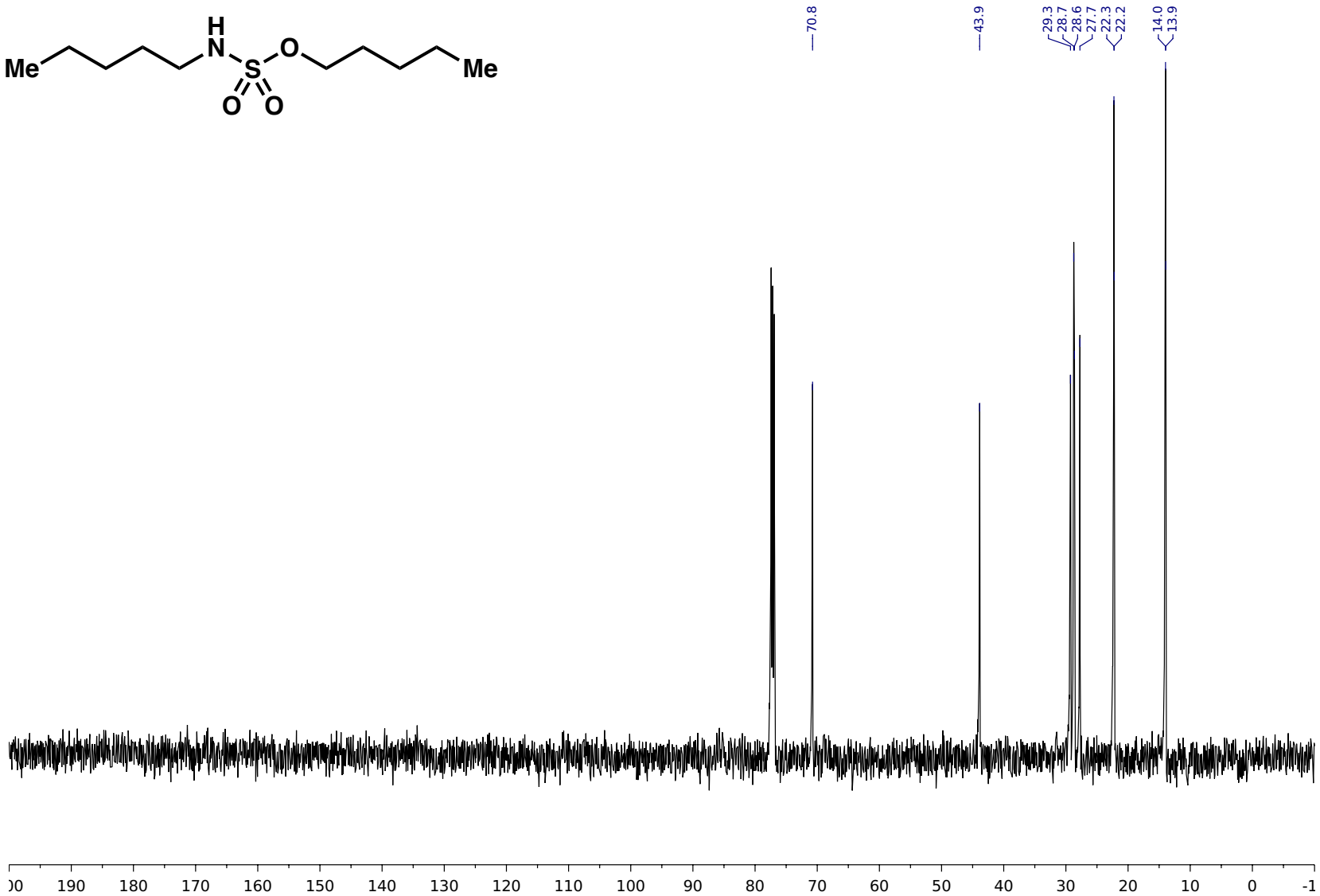
^{1}H NMR (400 MHz, $CDCl_3$) for pentyl cyclohexylsulfamate ester (**3f**)



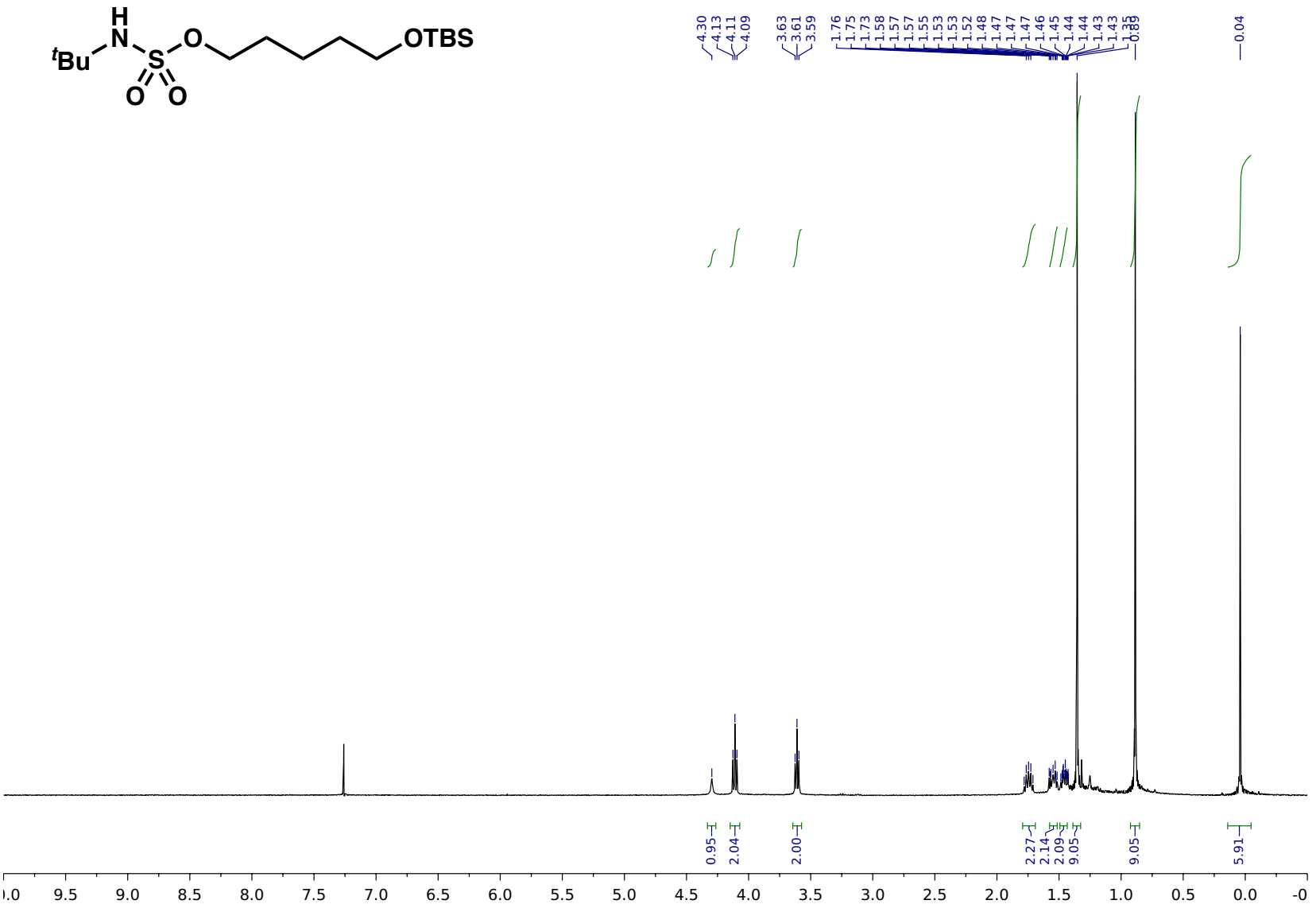
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for pentyl cyclohexylsulfamate ester (**3f**)



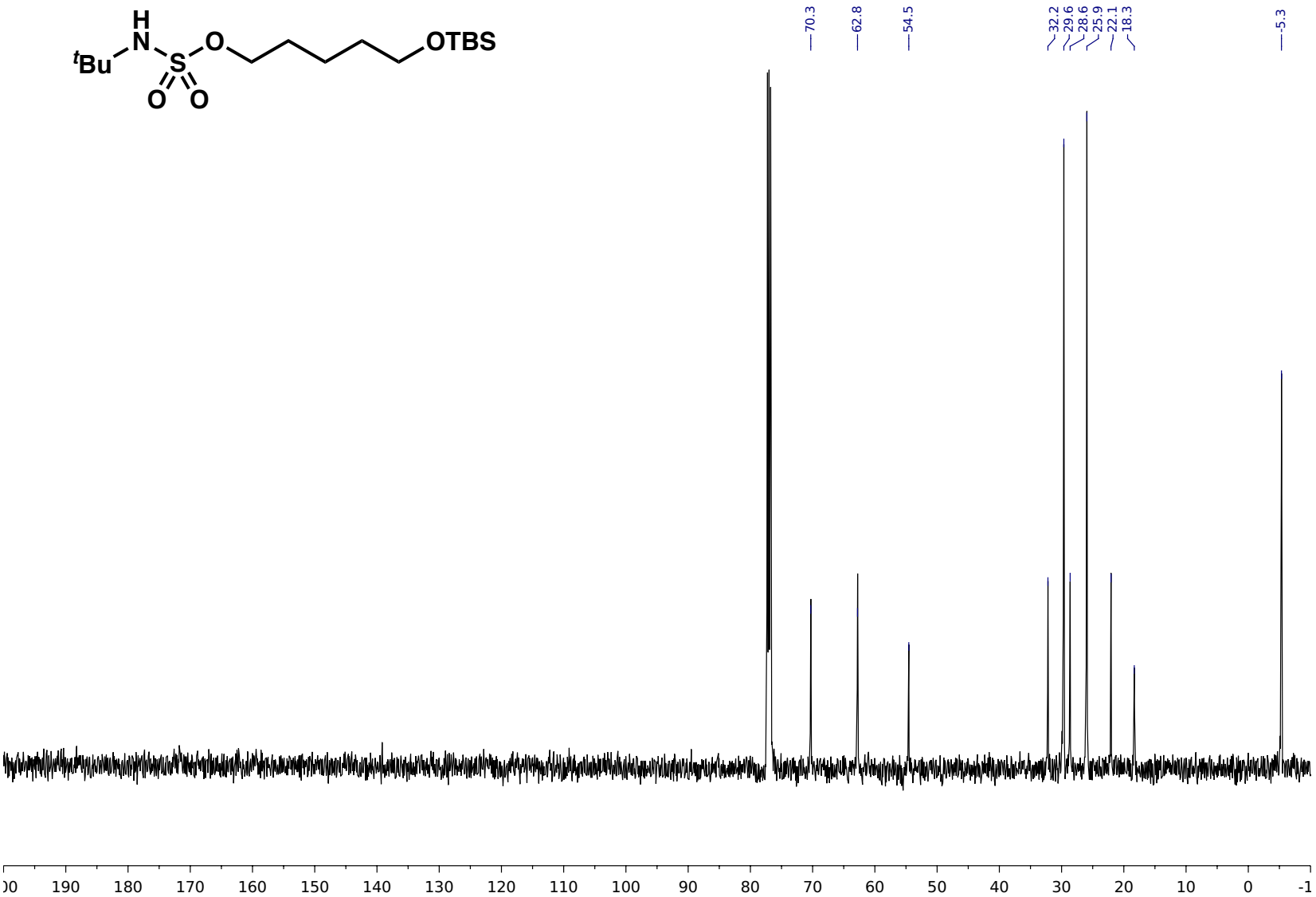
^{1}H NMR (400 MHz, $CDCl_3$) for pentyl pentylsulfamate ester (**3g**)



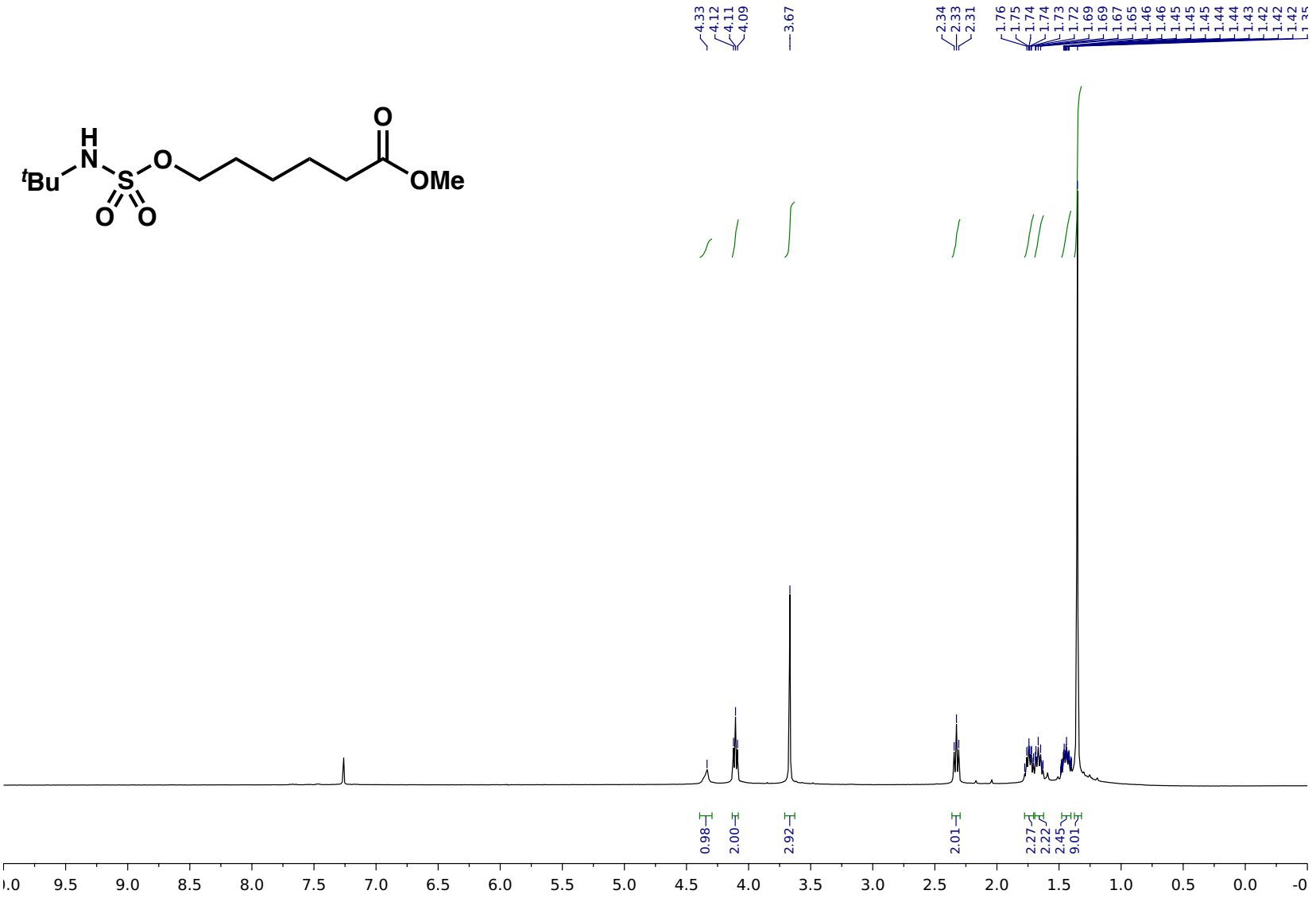
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for pentyl cyclohexylsulfamate ester (**3g**)



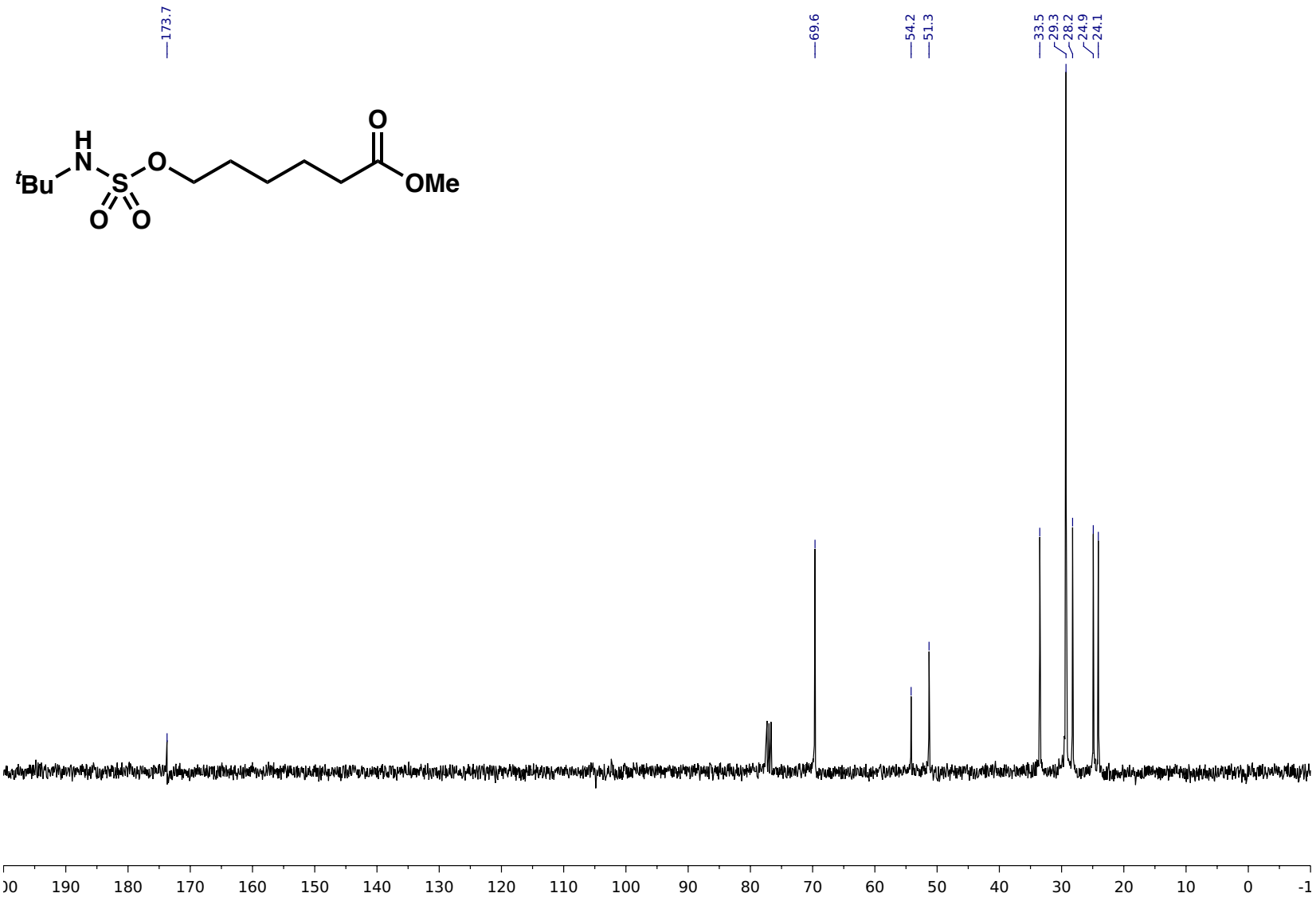
^{1}H NMR (400 MHz, $CDCl_3$) for 5-((tert-butyldimethylsilyl)oxy)pentyl tert-butylsulfamate ester (**3h**)



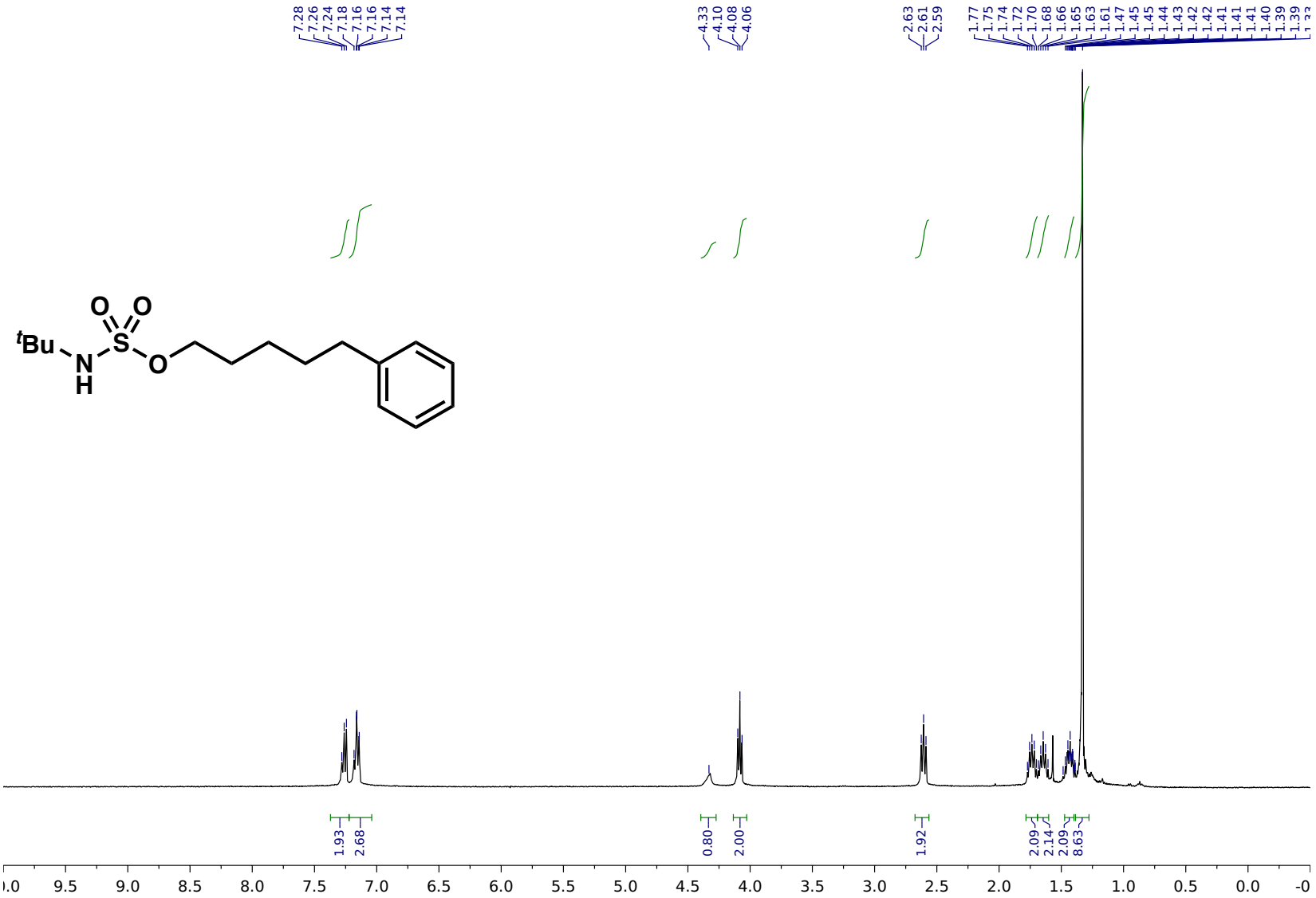
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 5-((tert-butyldimethylsilyl)oxy)pentyl *tert*-butylsulfamate ester (**3h**)



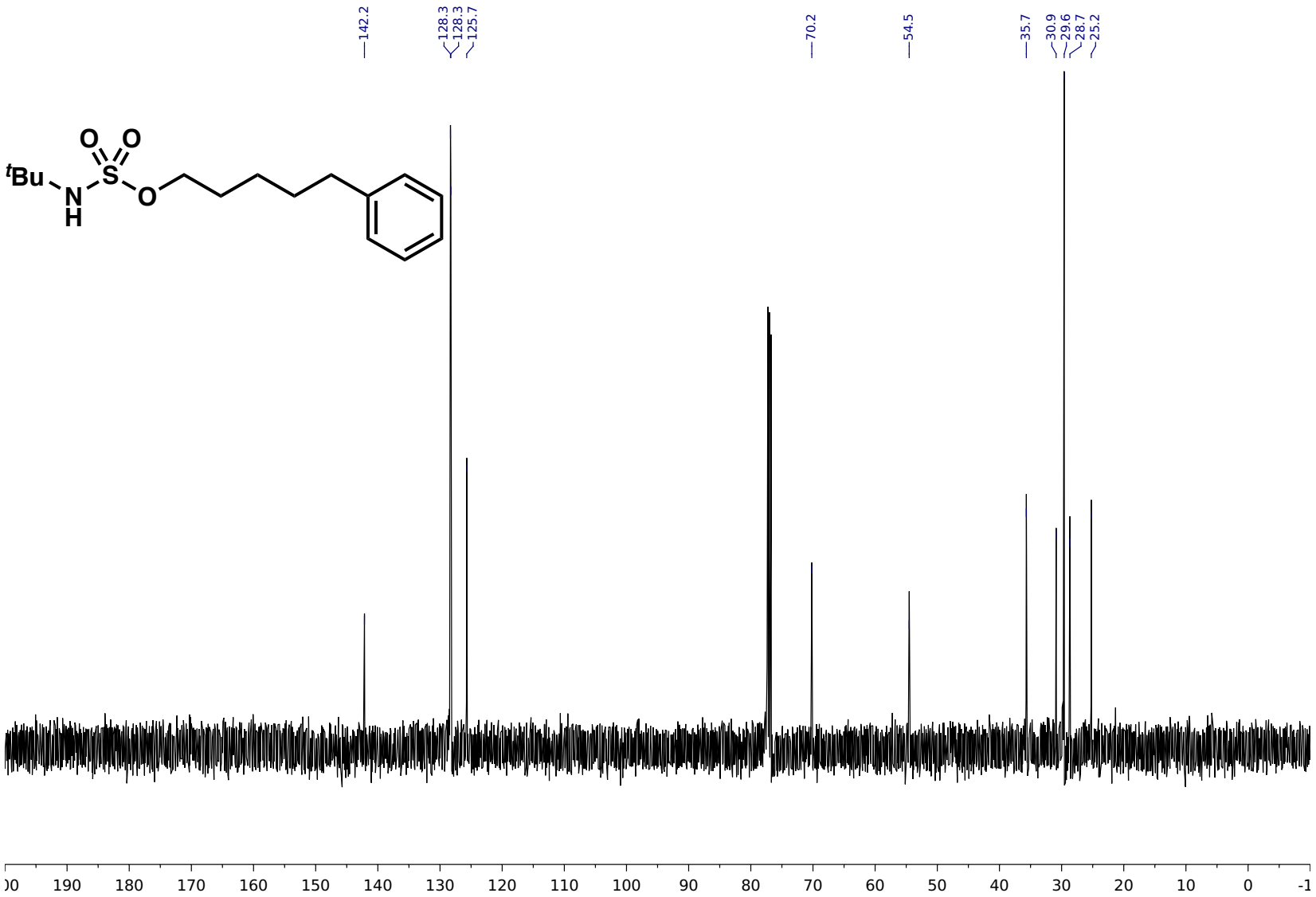
^{1}H NMR (400 MHz, $CDCl_3$) for methyl 6-hydroxyhexanoate *tert*-butylsulfamate ester (**3i**)



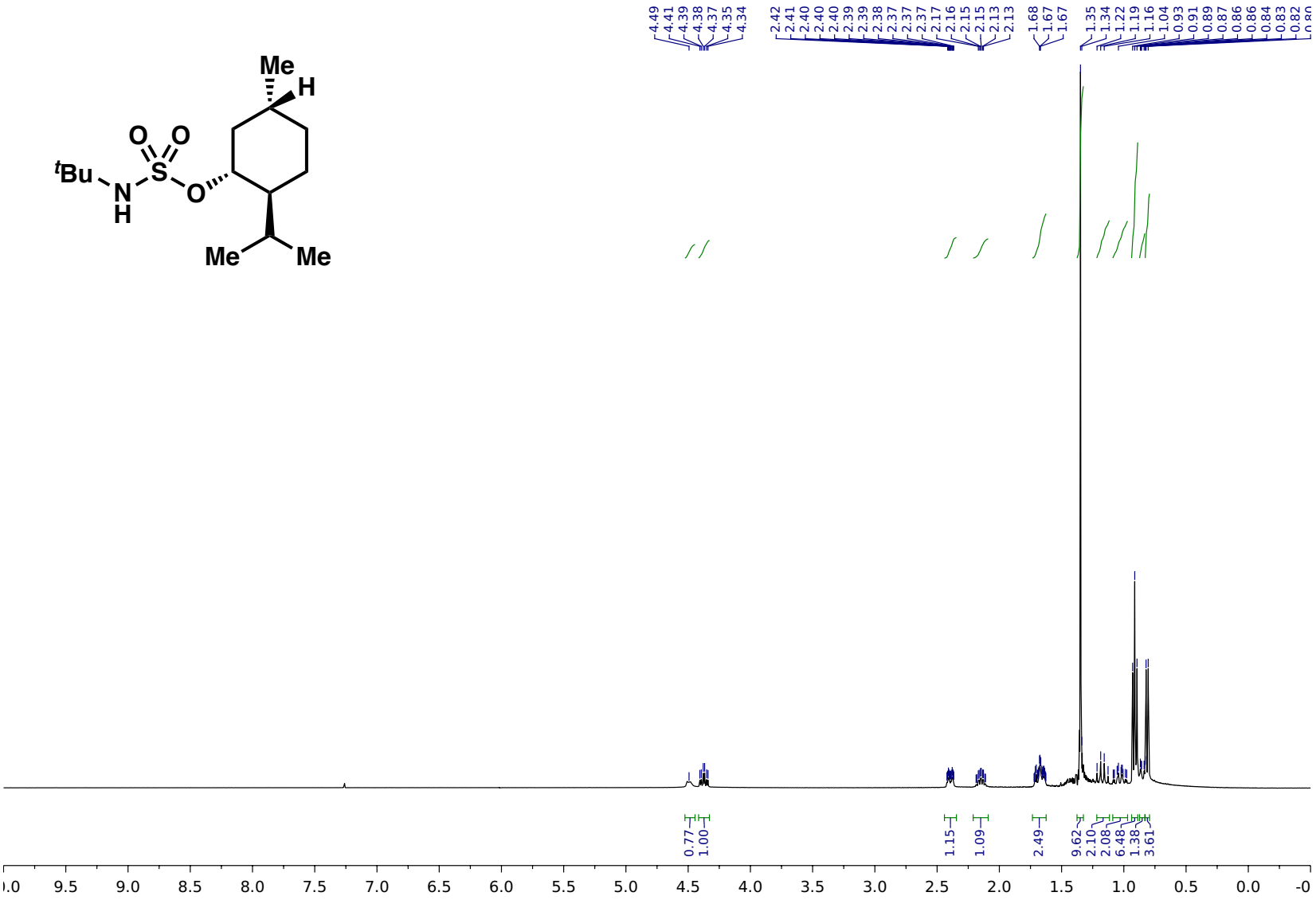
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for methyl 6-hydroxyhexanoate *tert*-butylsulfamate ester (**3i**)



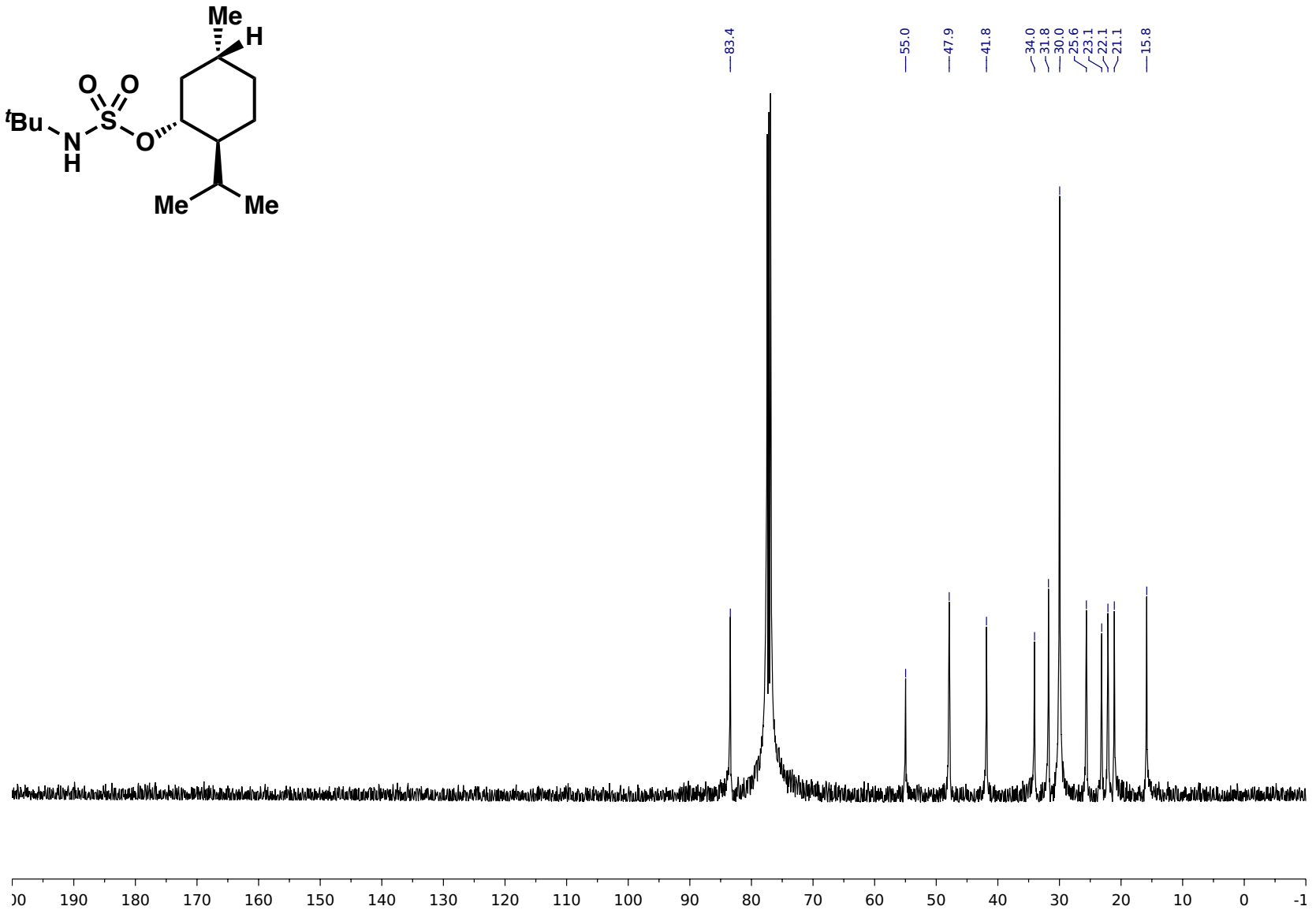
^{1}H NMR (400 MHz, $CDCl_3$) for 5-phenylpentyl tert-butylsulfamate ester (**3j**)



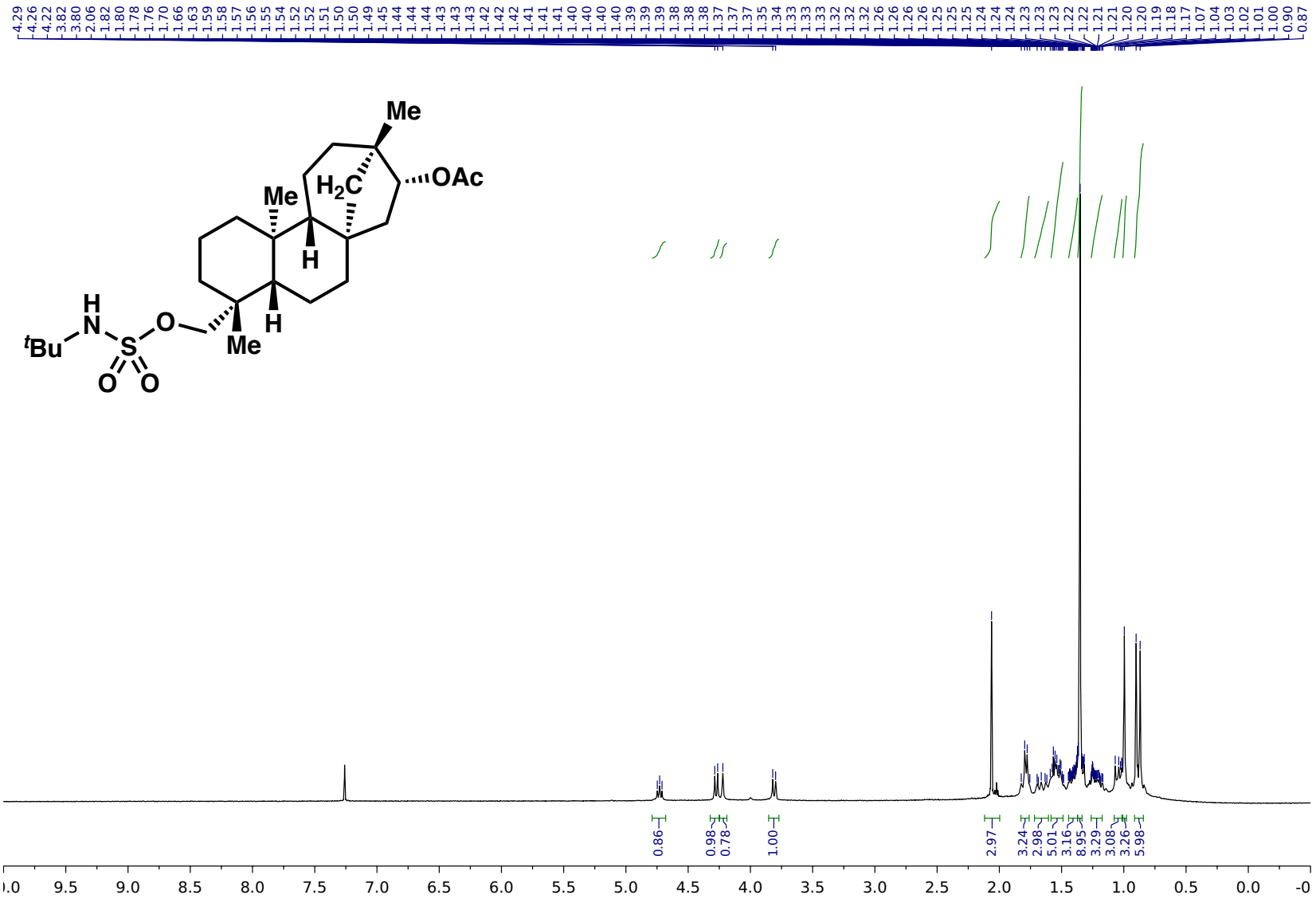
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 5-phenylpentyl *tert*-butylsulfamate ester (**3j**)



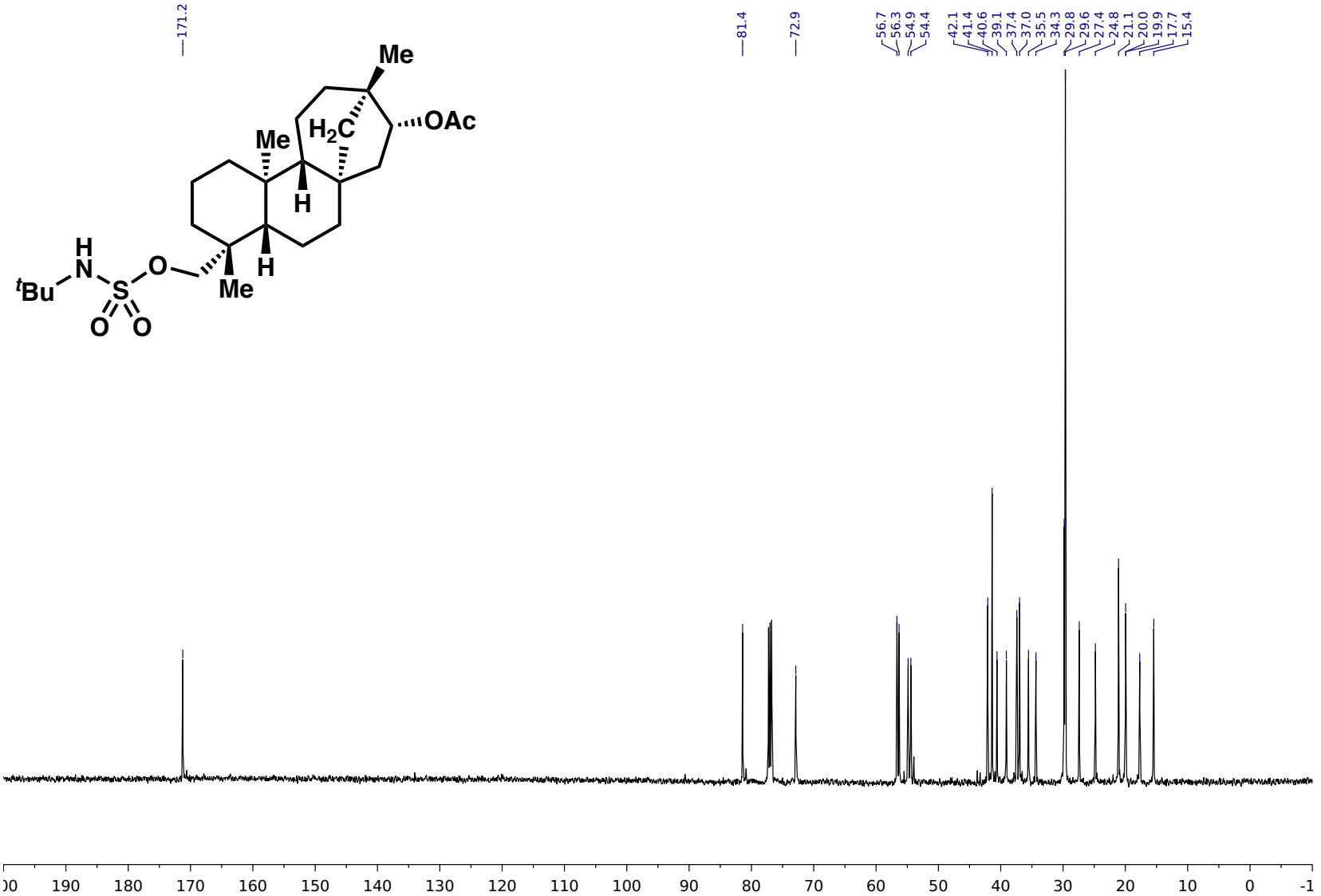
^{1}H NMR (400 MHz, $CDCl_3$) for (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl *tert*-butylsulfamate ester (**3m**)



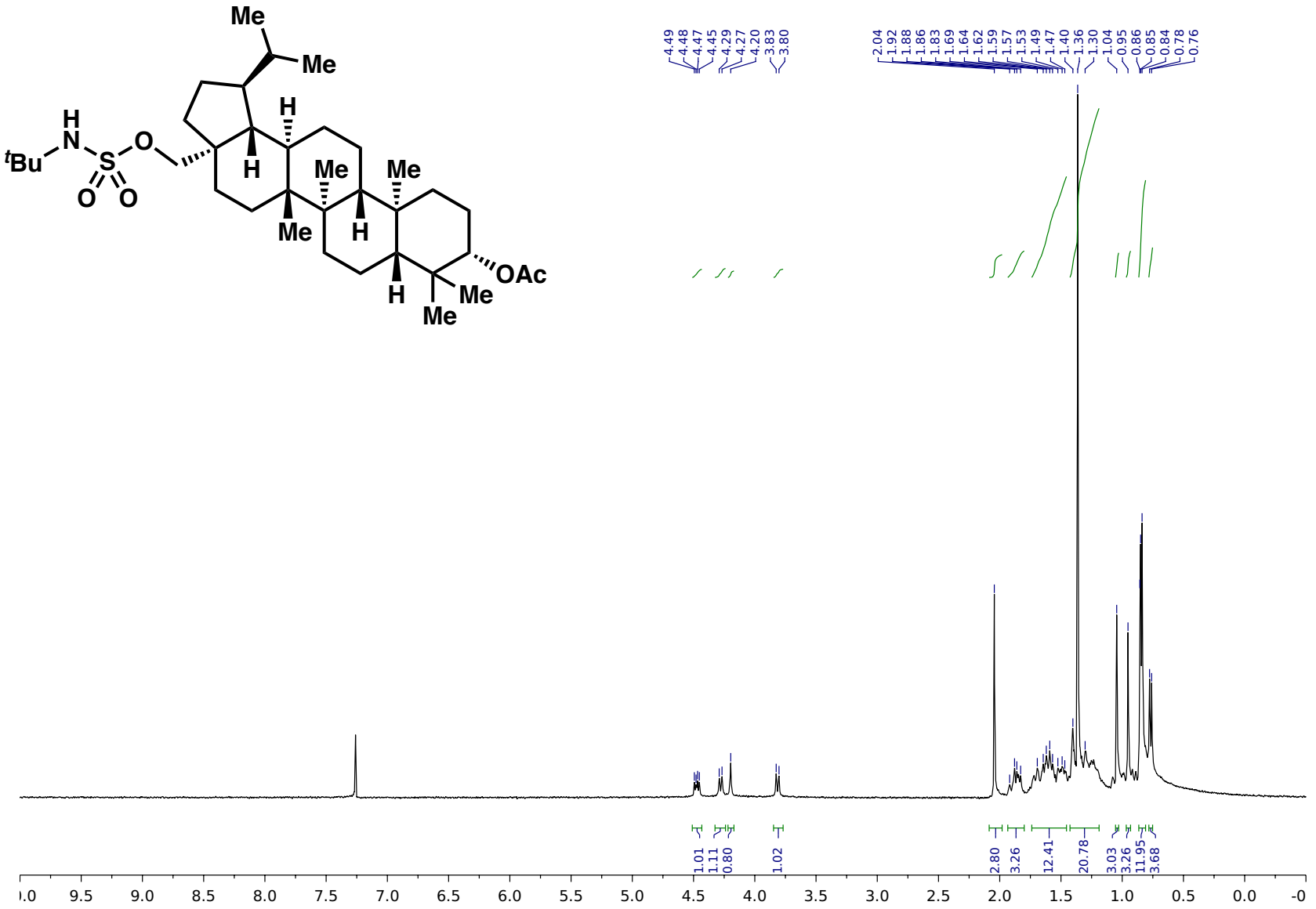
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl *tert*-butylsulfamate ester (**3m**)



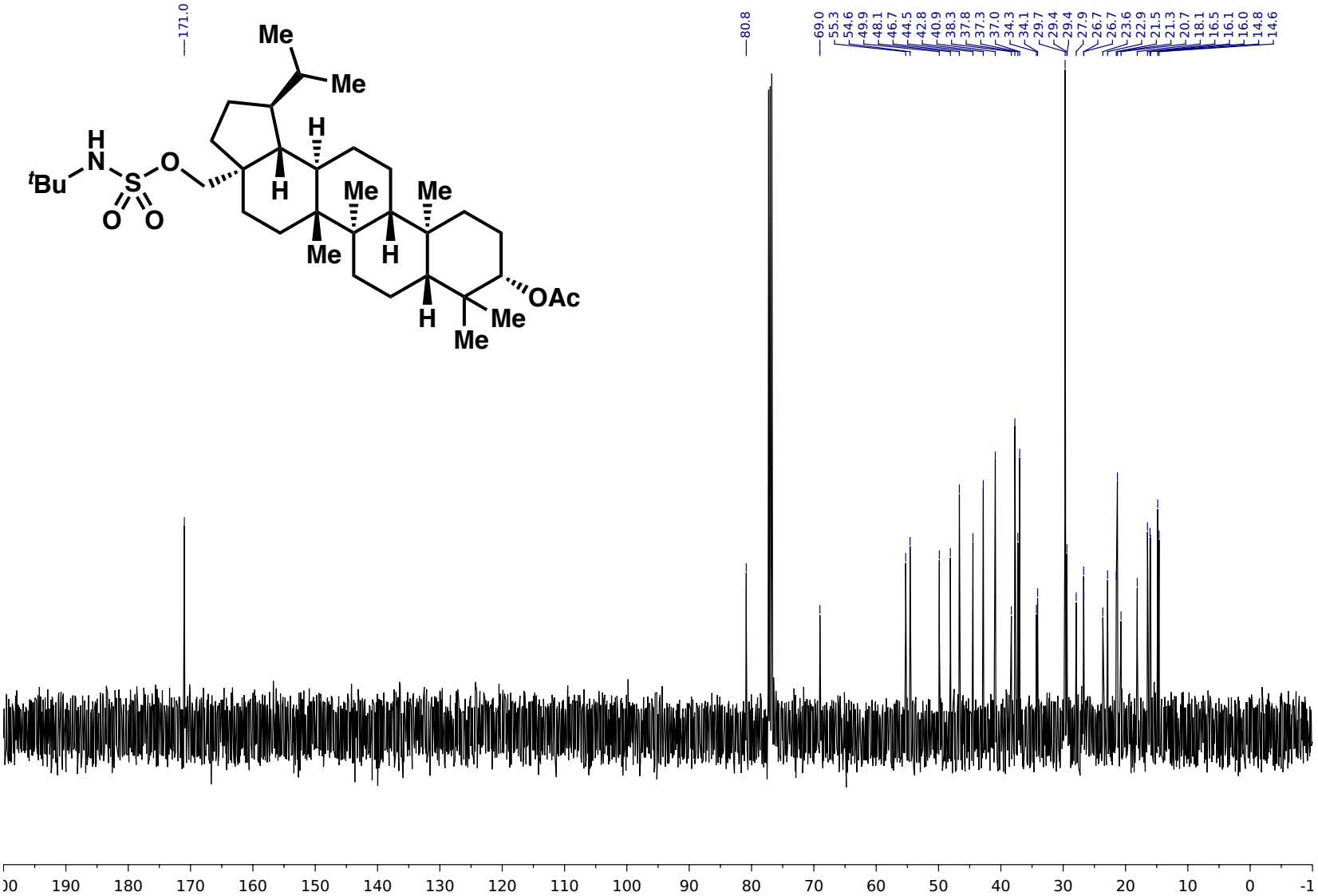
^{1}H NMR (400 MHz, $CDCl_3$) for (–)-16-acetoxy-13-methyl-17-norkaurane *tert*-butylsulfamate (**3p**)



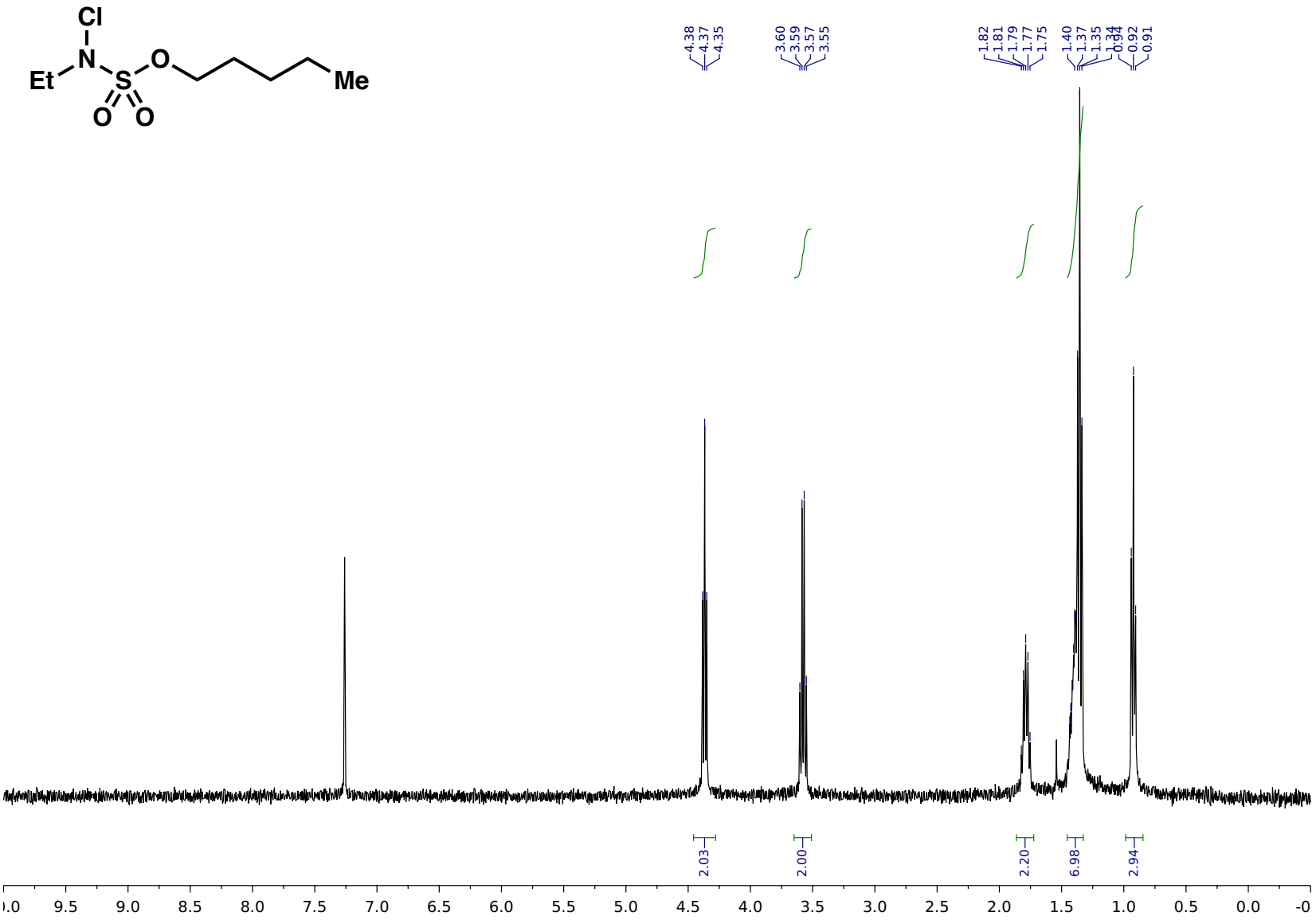
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for (–)-16-acetoxy-13-methyl-17-norkaurane *tert*-butylsulfamate (**3p**)



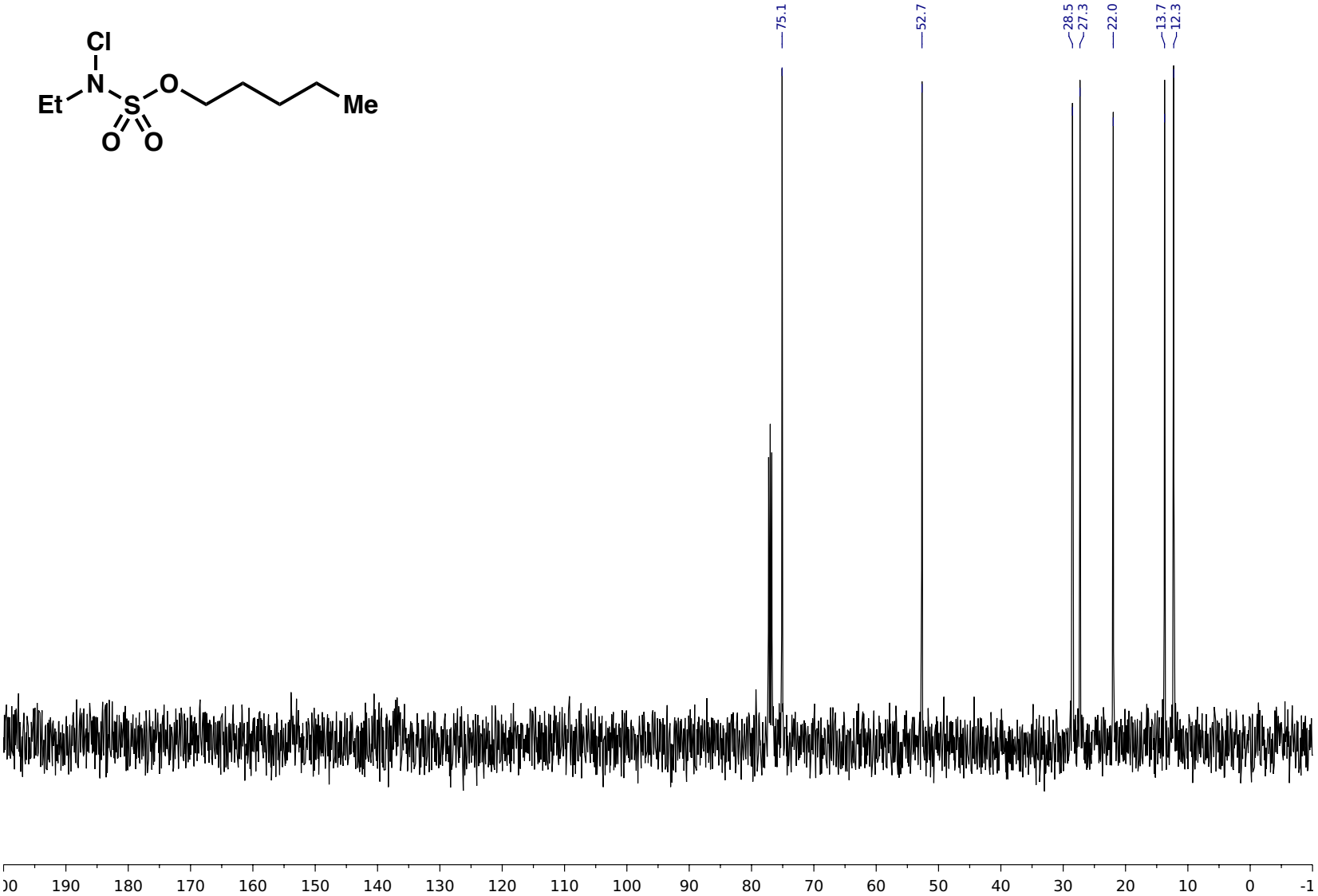
^{1}H NMR (400 MHz, $CDCl_3$) for 3-acetoxydihydrobetulinic *tert*-butylsulfamate (**3q**)



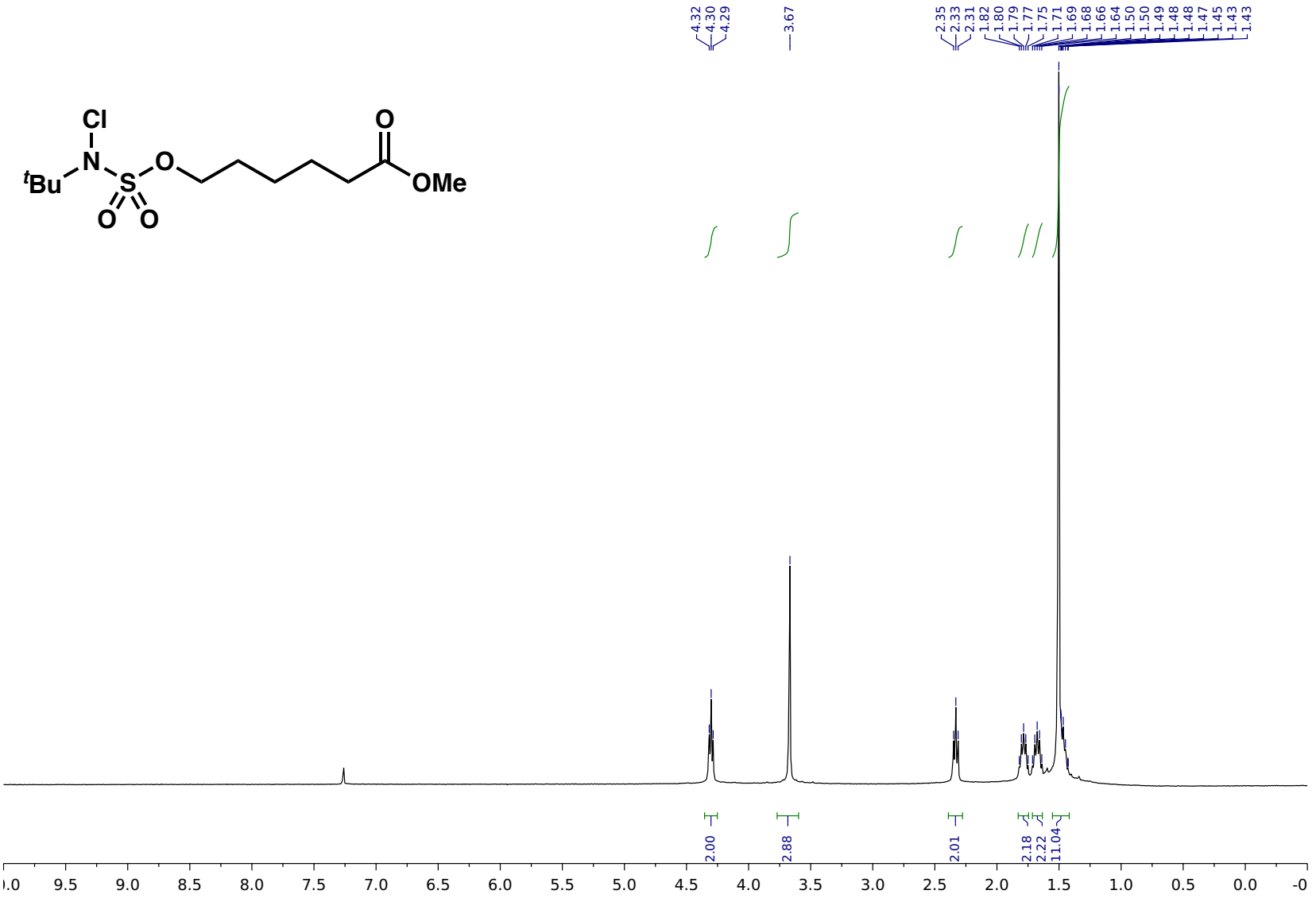
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-acetoxydihydrobetulinic *tert*-butylsulfamate (**3q**)



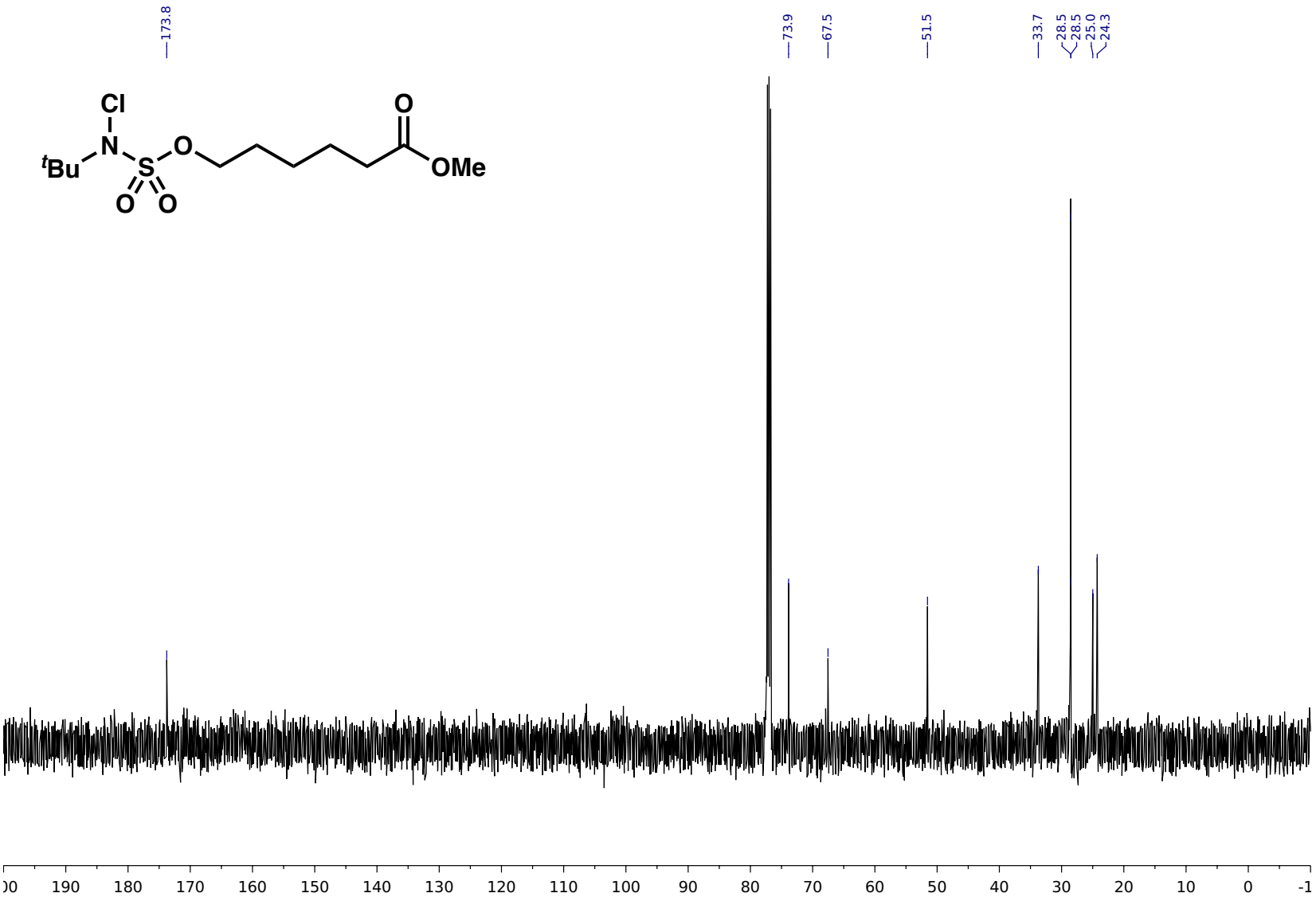
^{1}H NMR (400 MHz, $CDCl_3$) for pentyl ethylchlorosulfamate ester (**S1b**)



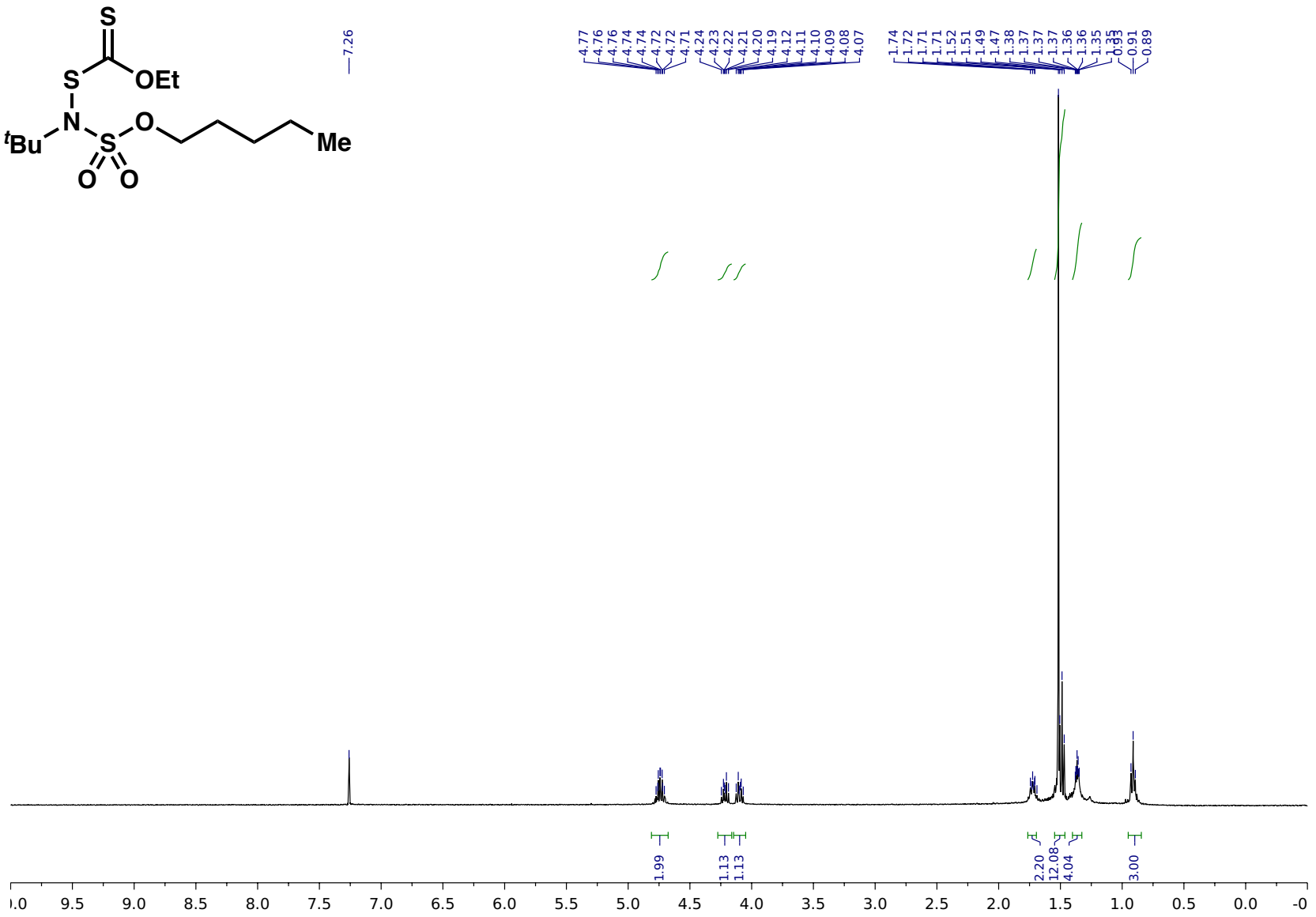
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for pentyl ethylchlorosulfamate ester (**S1b**)



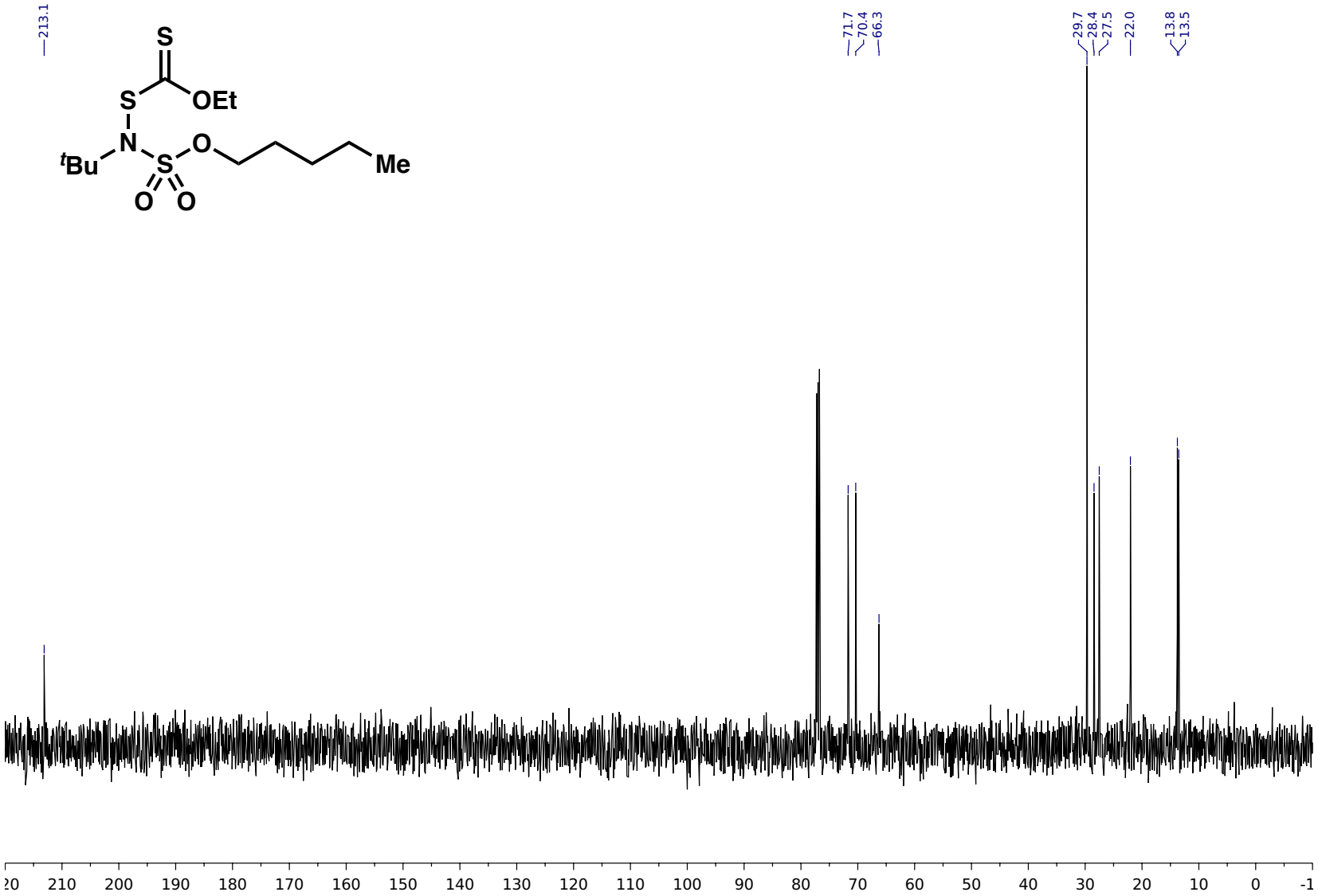
^{1}H NMR (400 MHz, $CDCl_3$) for methyl 6-hydroxyhexanoate *tert*-butylchlorosulfamate ester (**S1i**)



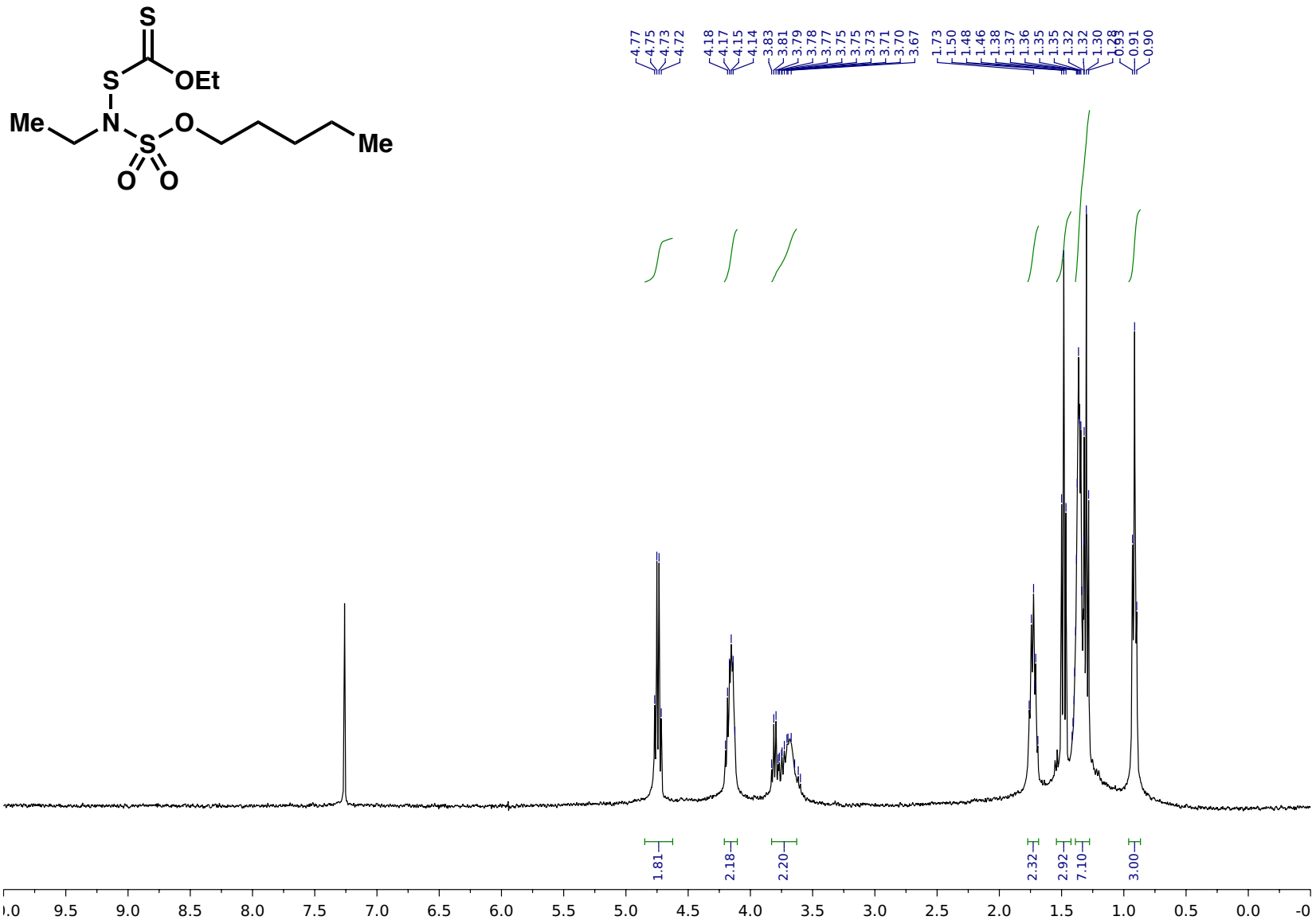
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for methyl 6-hydroxyhexanoate *tert*-butylchlorosulfamate ester (**S1i**)



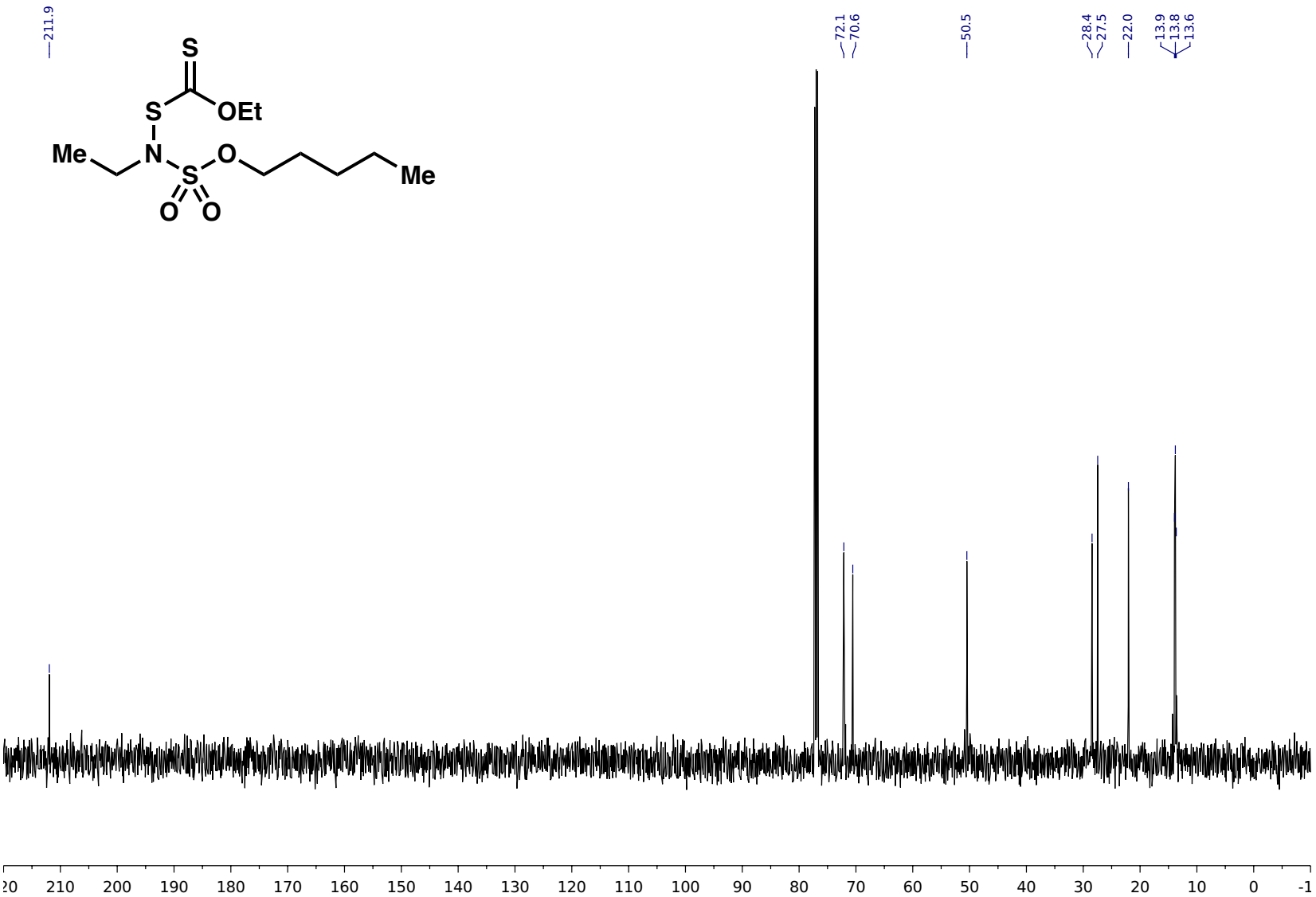
^{1}H NMR (400 MHz, $CDCl_3$) for pentyl *tert*-butyl((ethoxycarbonothioyl)thio))sulfamate (**1a**) [prepared by general procedure E]



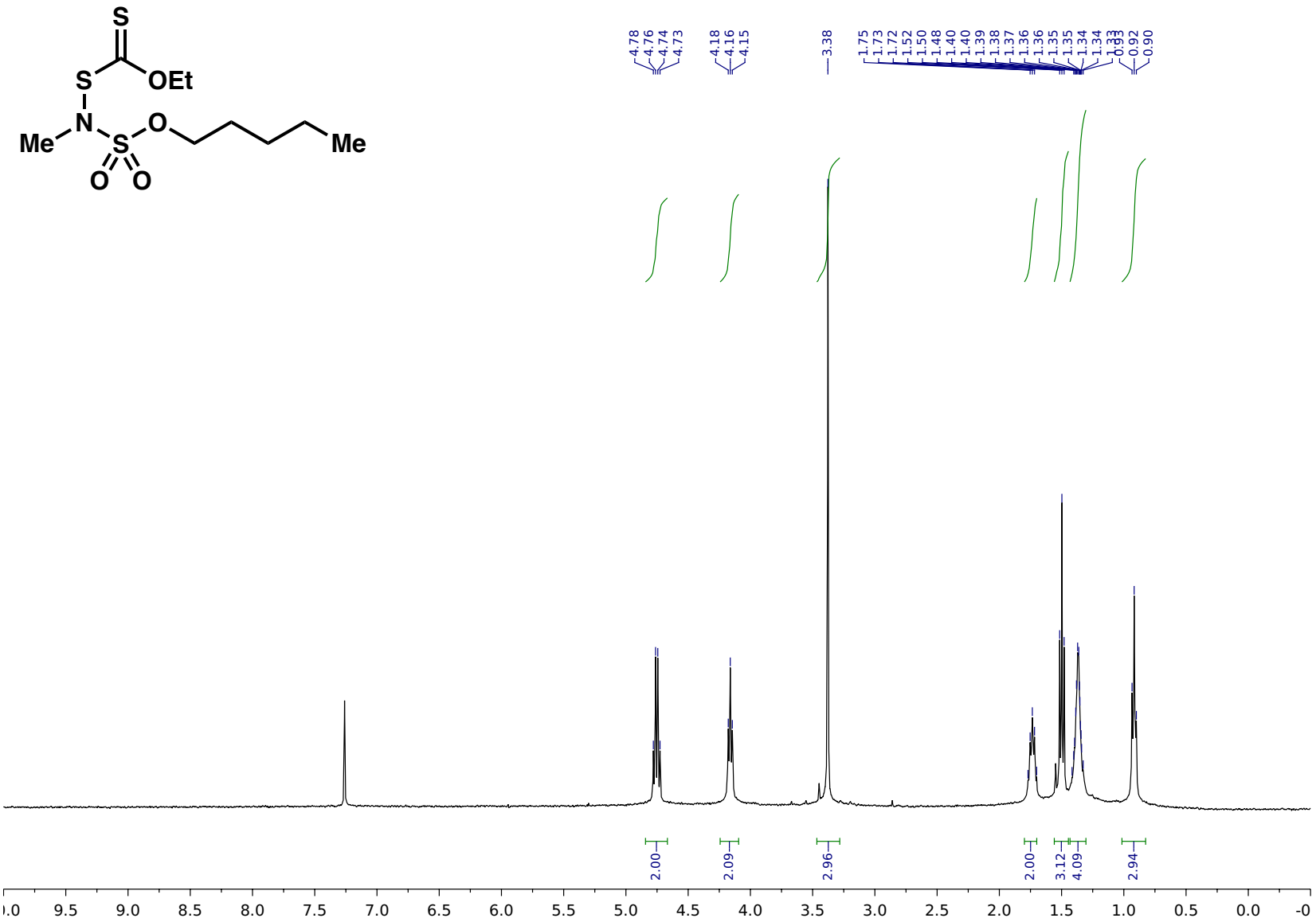
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for pentyl *tert*-butyl((ethoxycarbonothioyl)thio))sulfamate (**1a**) [prepared by general procedure E]



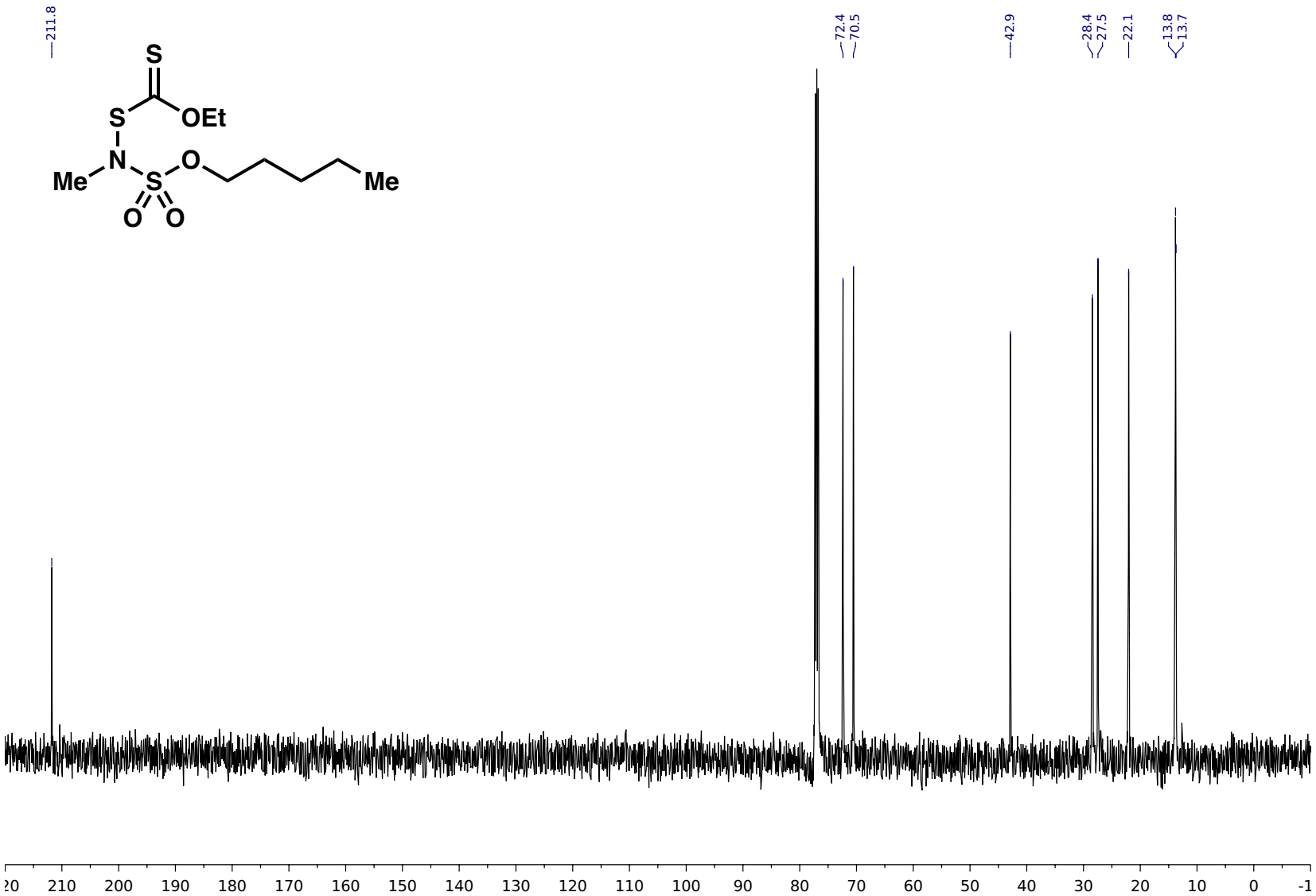
^{1}H NMR (400 MHz, $CDCl_3$) for pentyl ethyl((ethoxycarbonothioyl)thio))sulfamate (**1b**) [prepared by general procedure E]



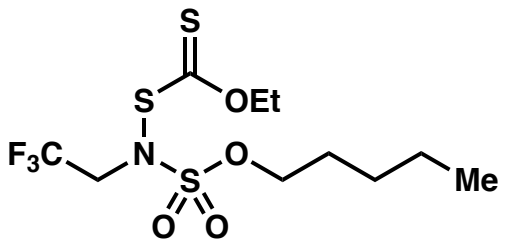
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for pentyl ethyl((ethoxycarbonothioyl)thio))sulfamate (**1b**) [prepared by general procedure E]



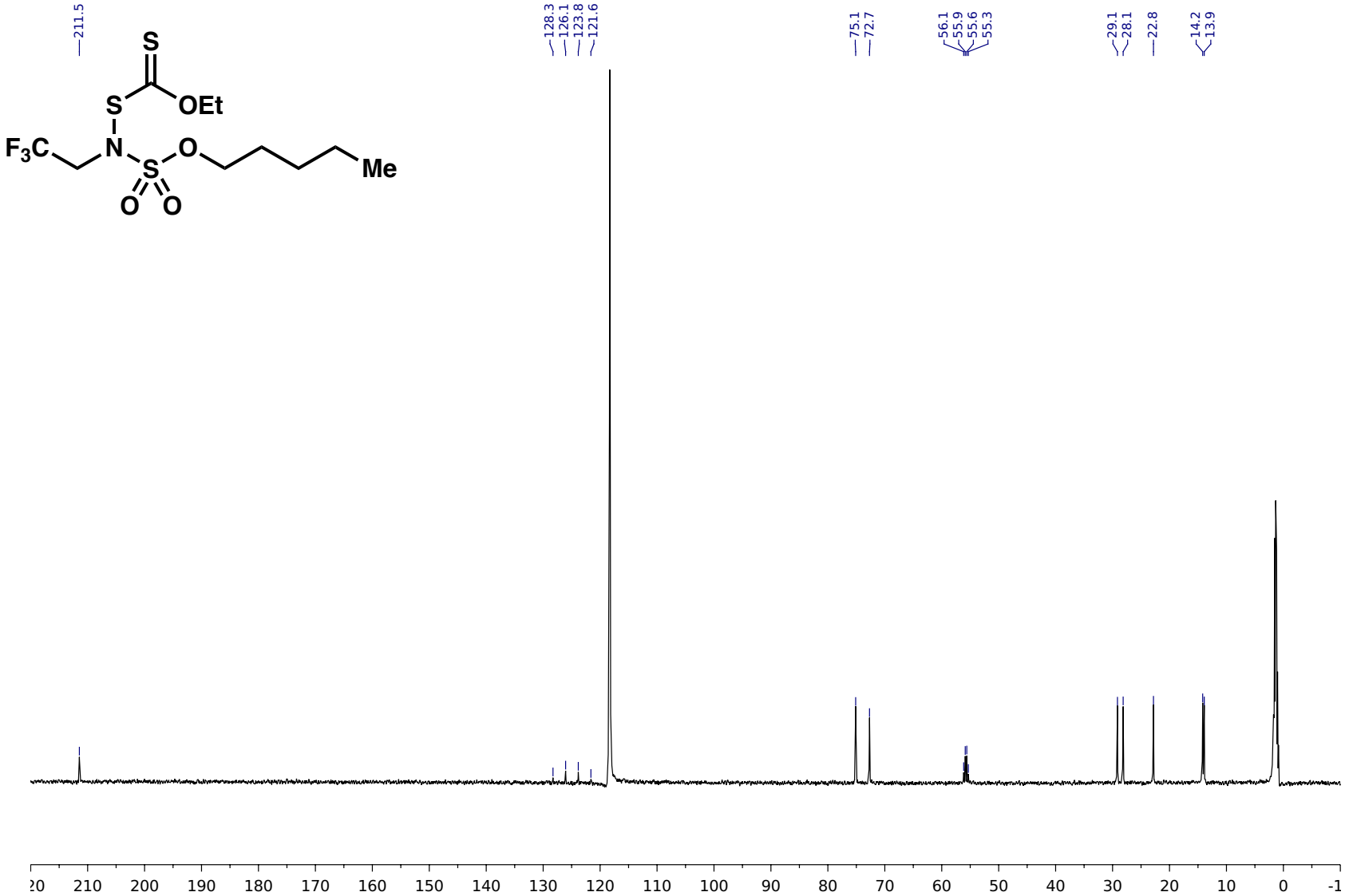
^{1}H NMR (400 MHz, $CDCl_3$) for pentyl methyl((ethoxycarbonothioyl)thio))sulfamate (**1c**)



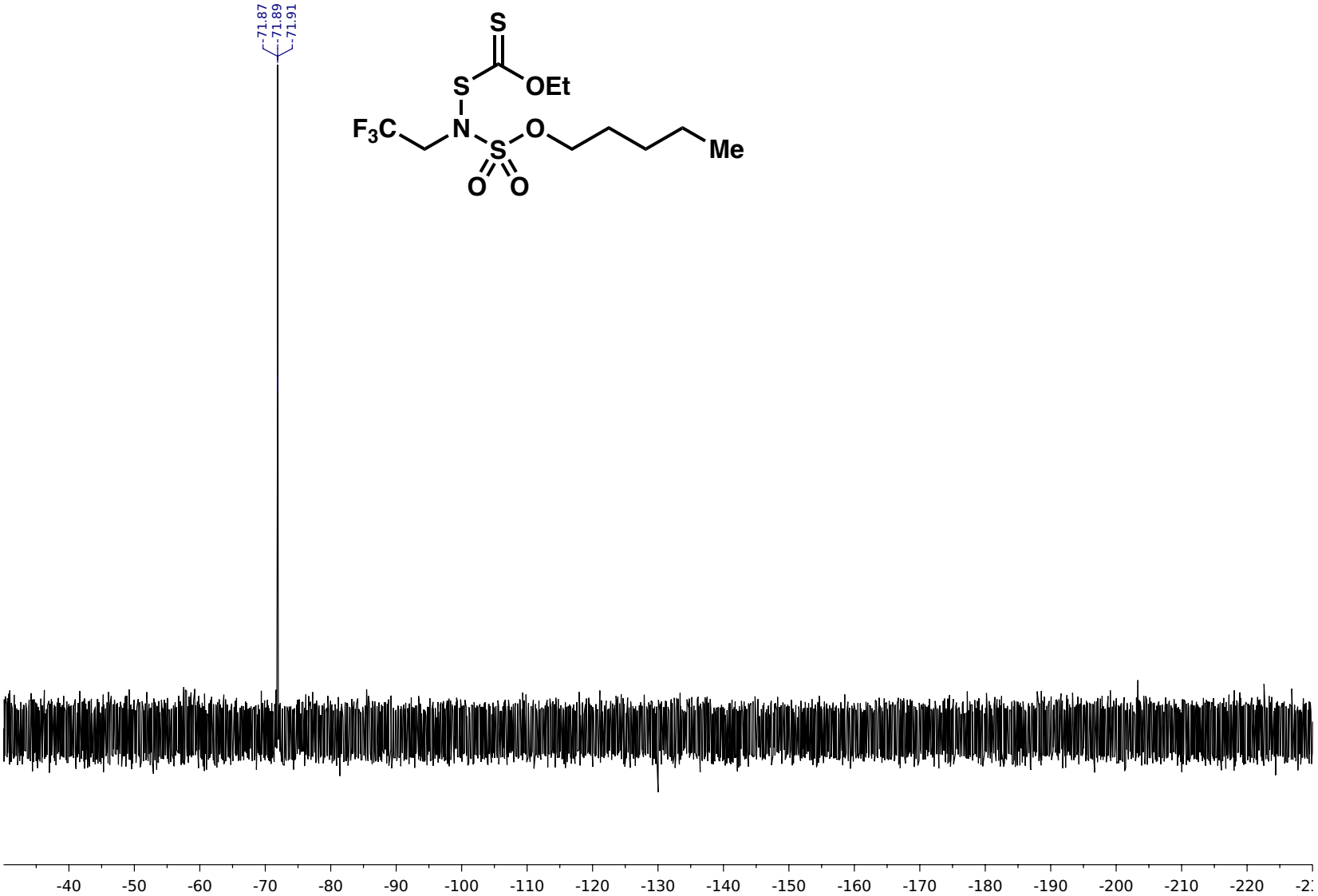
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for pentyl methyl((ethoxycarbonothioyl)thio))sulfamate (**1c**)



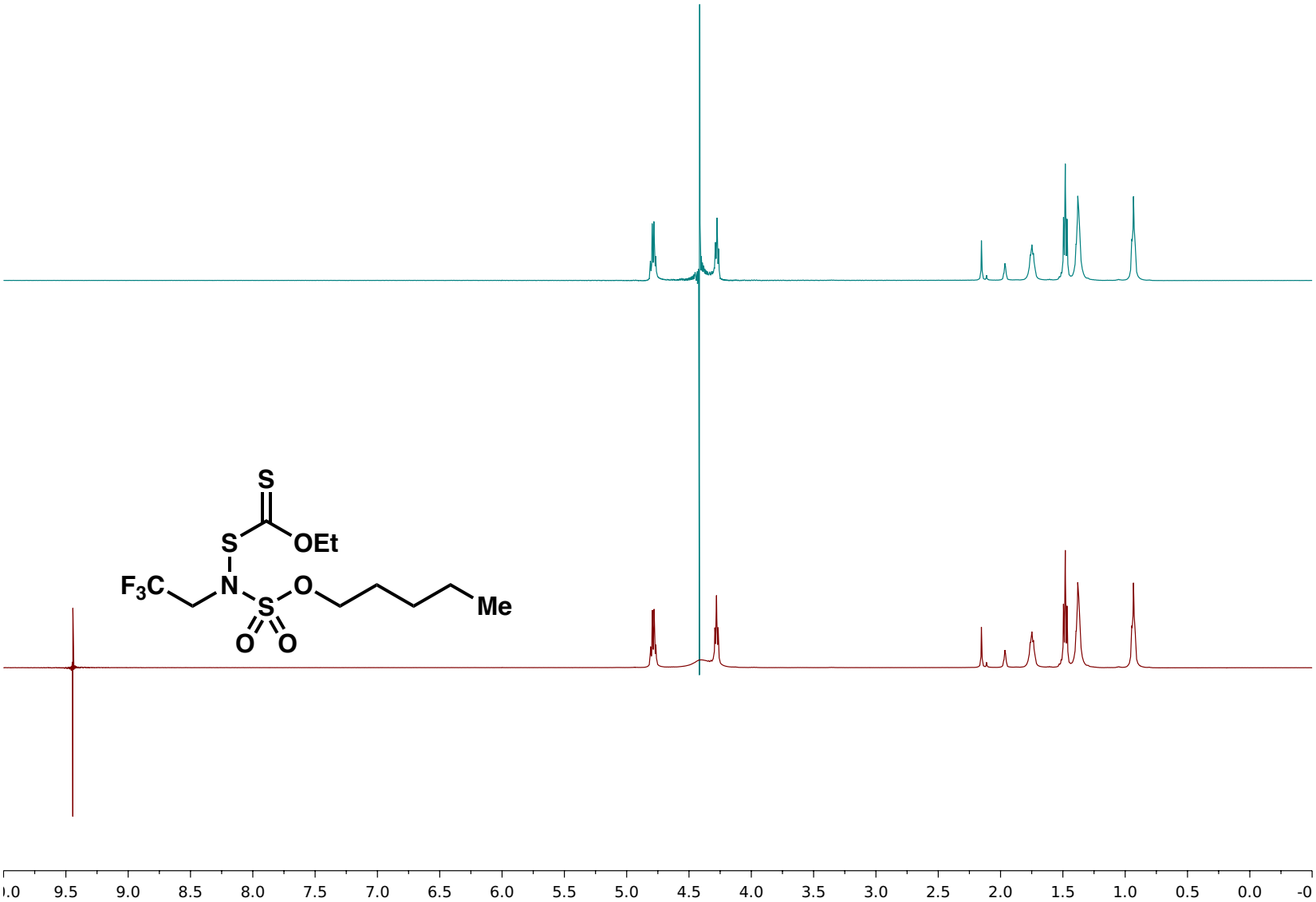
^{1}H NMR (400 MHz, CD_3CN) for pentyl (2,2,2-trifluoroethyl((ethoxycarbonothioyl)thio))sulfamate (**1d**)



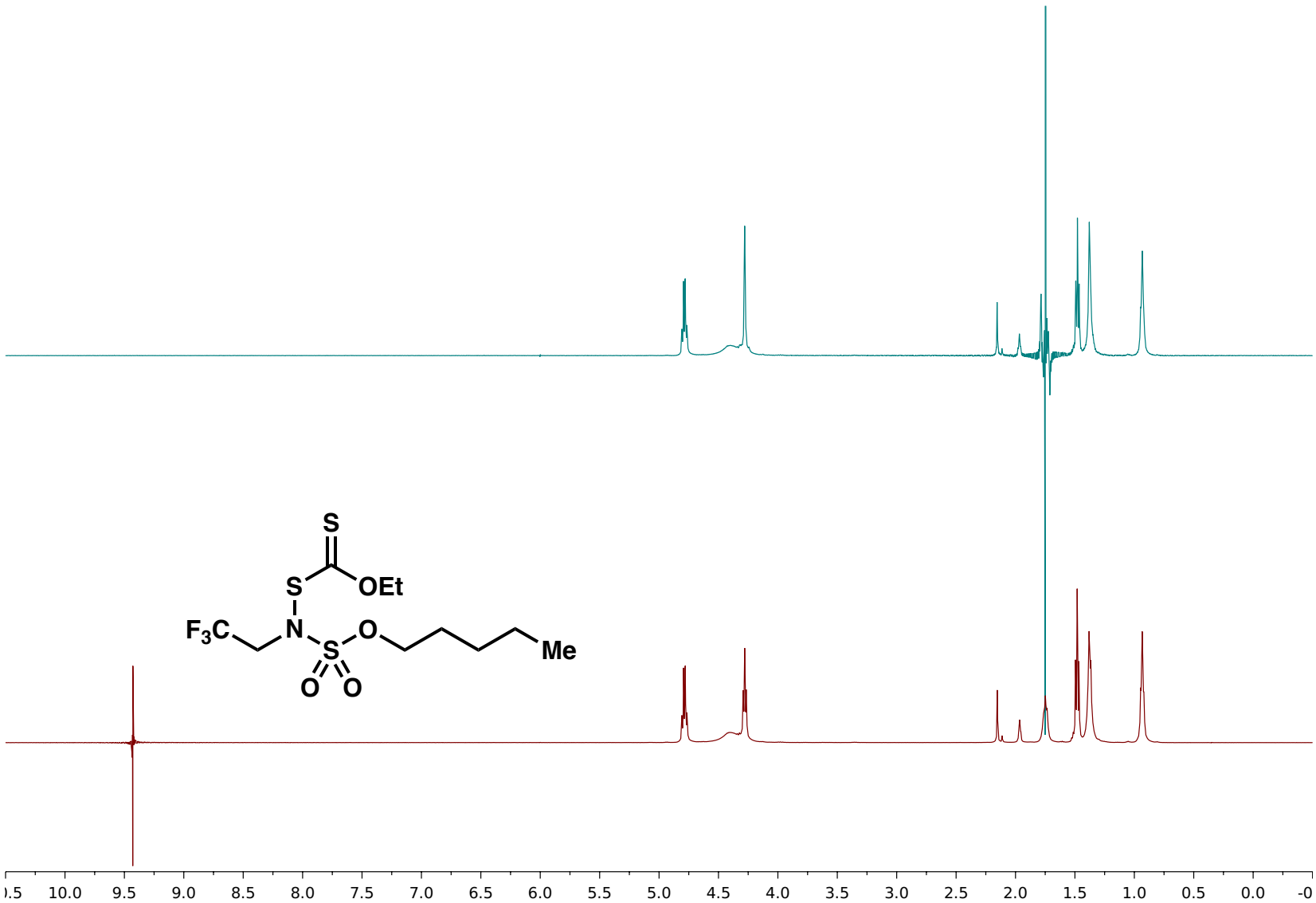
$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3CN) for pentyl (2,2,2-trifluoroethyl((ethoxycarbonothioyl)thio))sulfamate (**1d**)



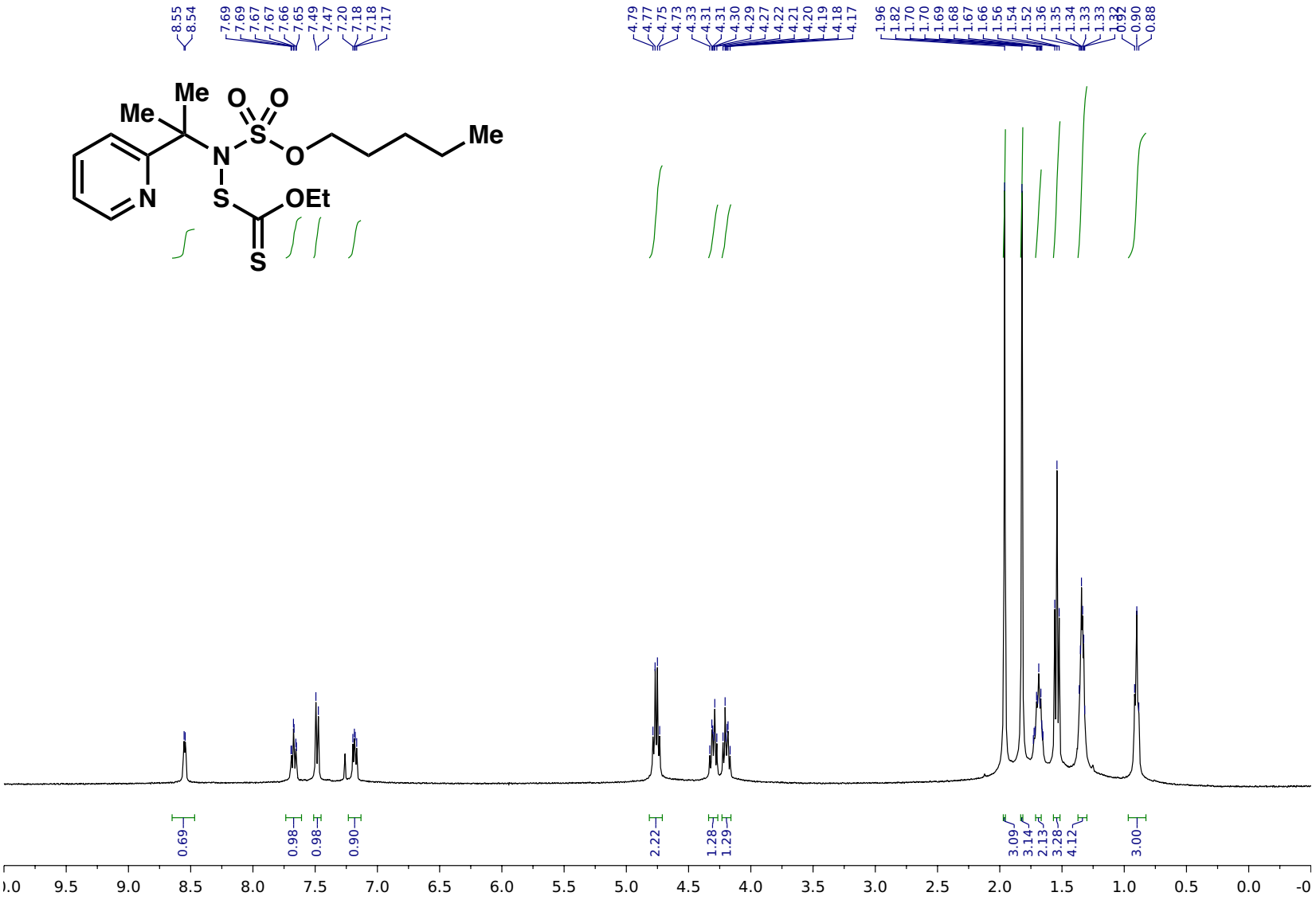
^{19}F NMR (376 MHz, $CDCl_3$) for pentyl (2,2,2-trifluoroethyl((ethoxycarbonothioyl)thio))sulfamate (**1d**)



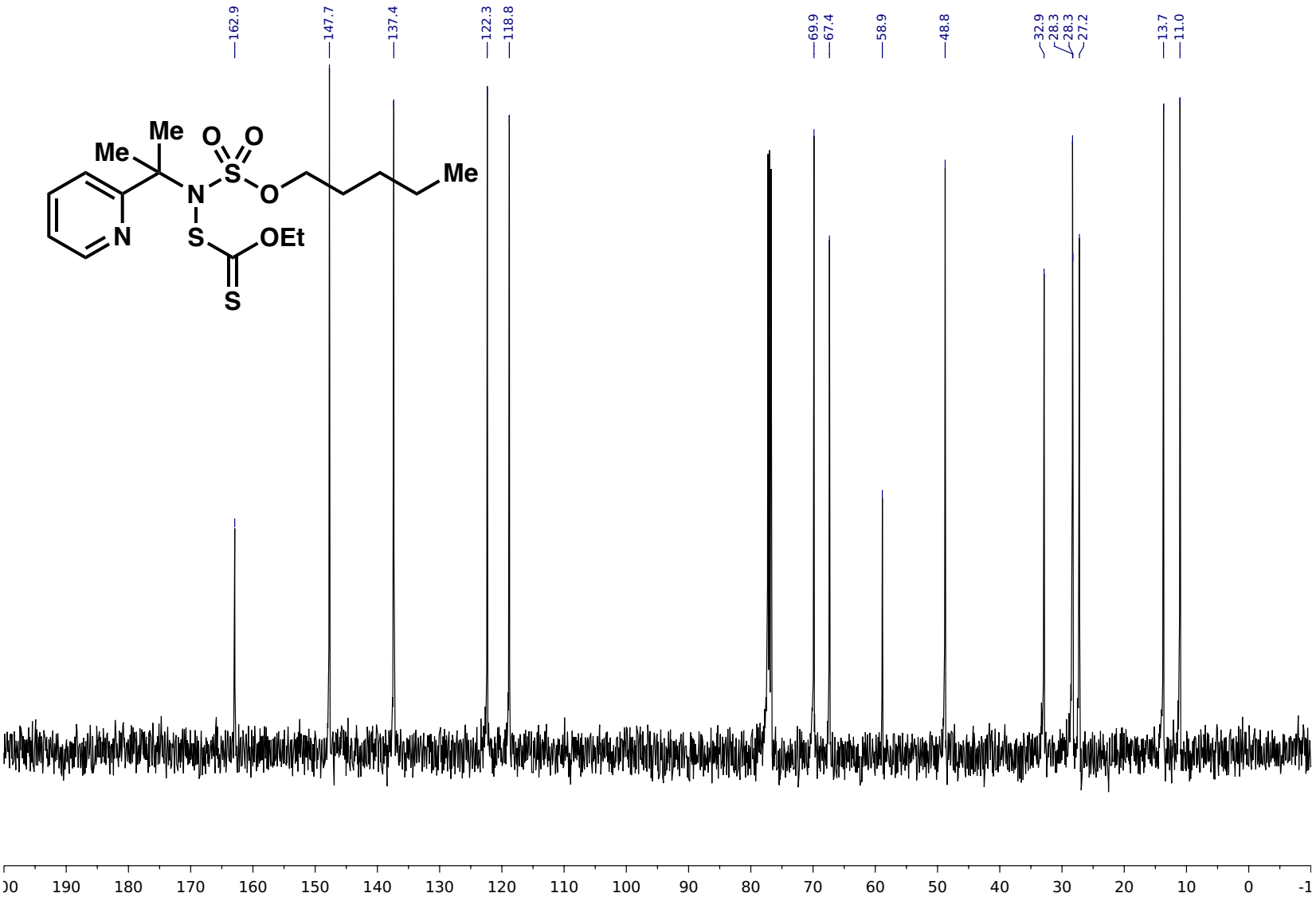
Homonuclear decoupling experiment for (**1d**) [Bottom: Control Vs Top: Irradiation @ 4.4 ppm]



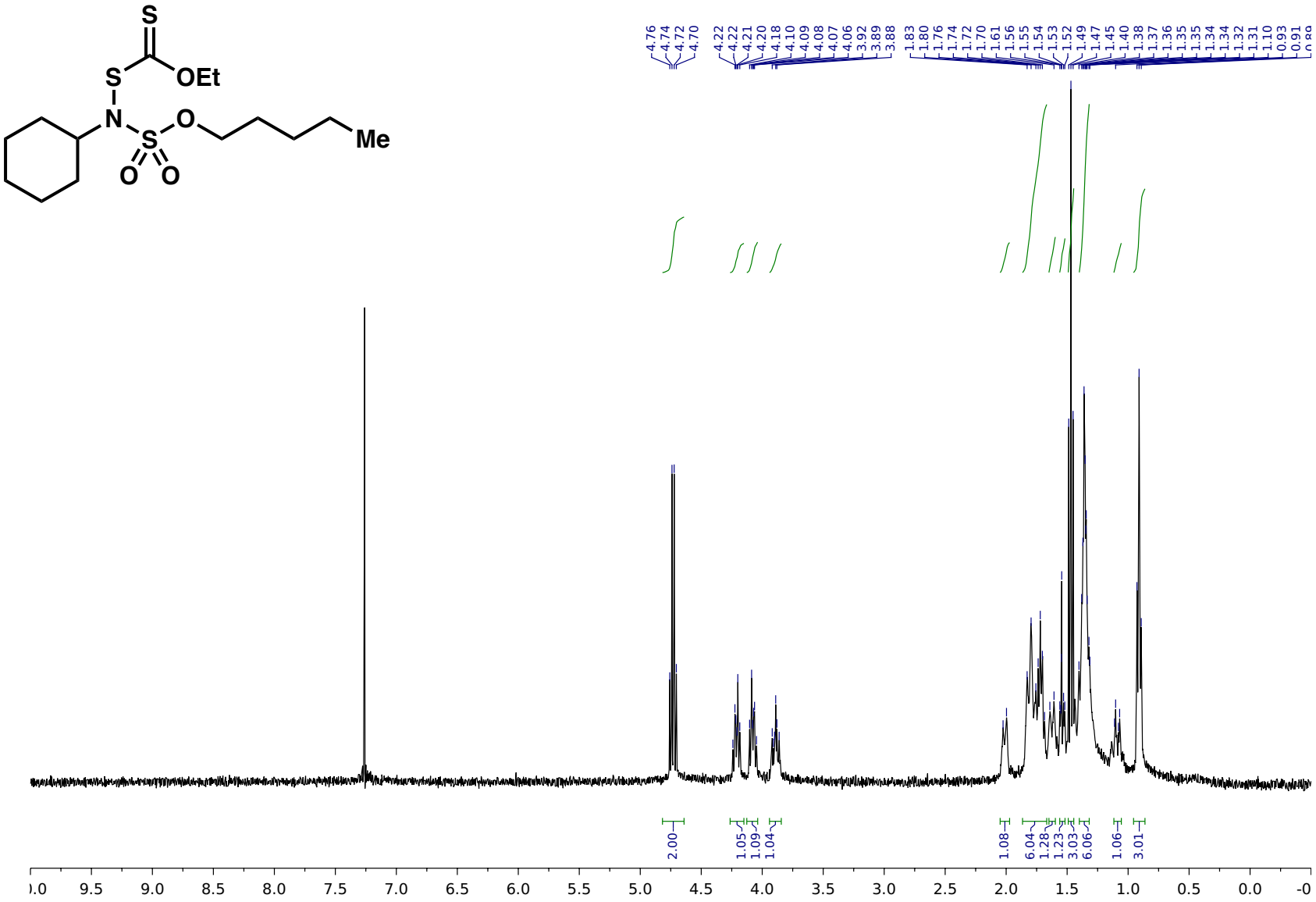
Homonuclear decoupling experiment for (**1d**) [Bottom: Control Vs Top: Irradiation @ 1.75 ppm]



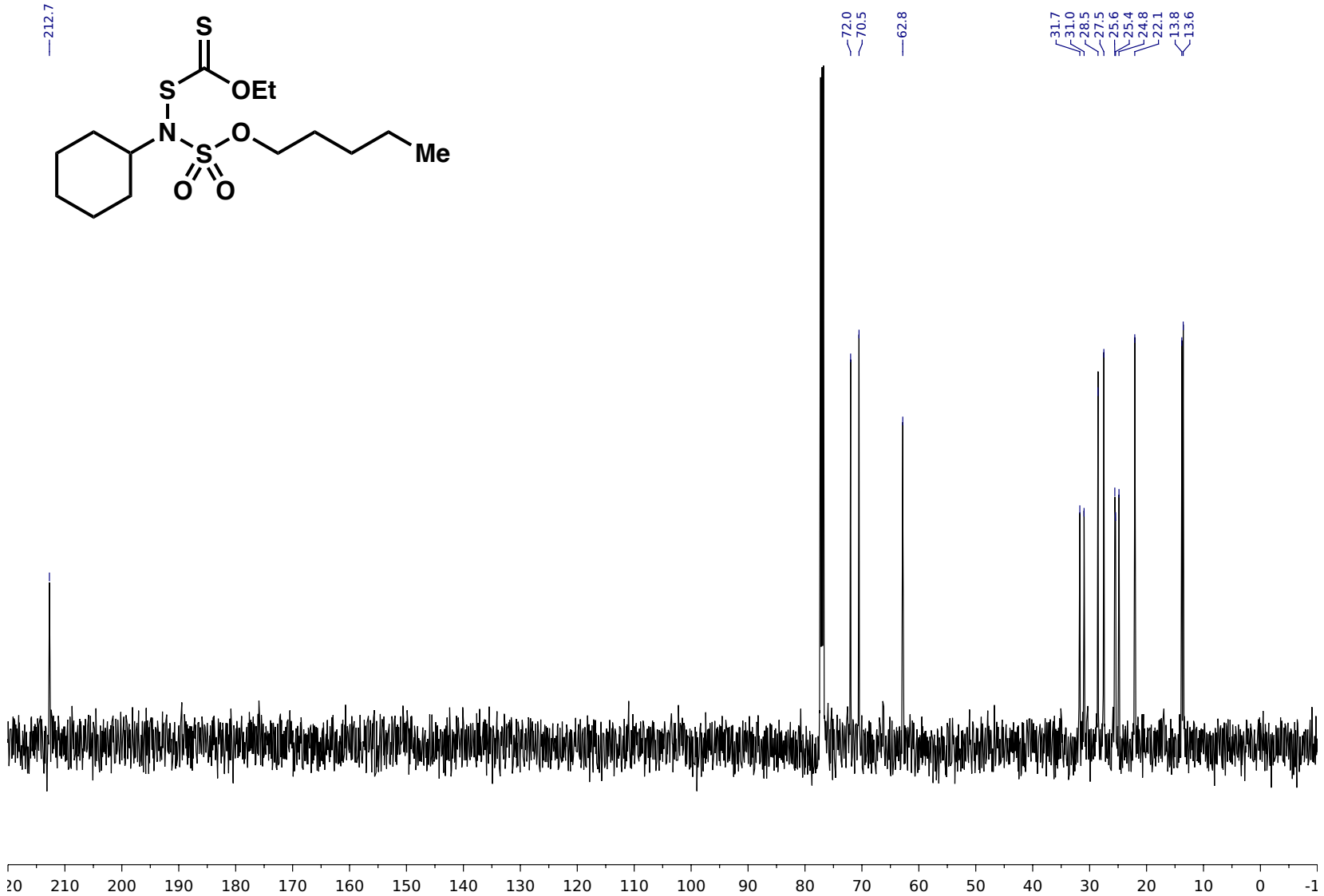
^{1}H NMR (400 MHz, $CDCl_3$) for pentyl 2-(pyridine-2-yl)propan-2-yl) ((ethoxycarbonothioyl)thio))sulfamate (**1e**)



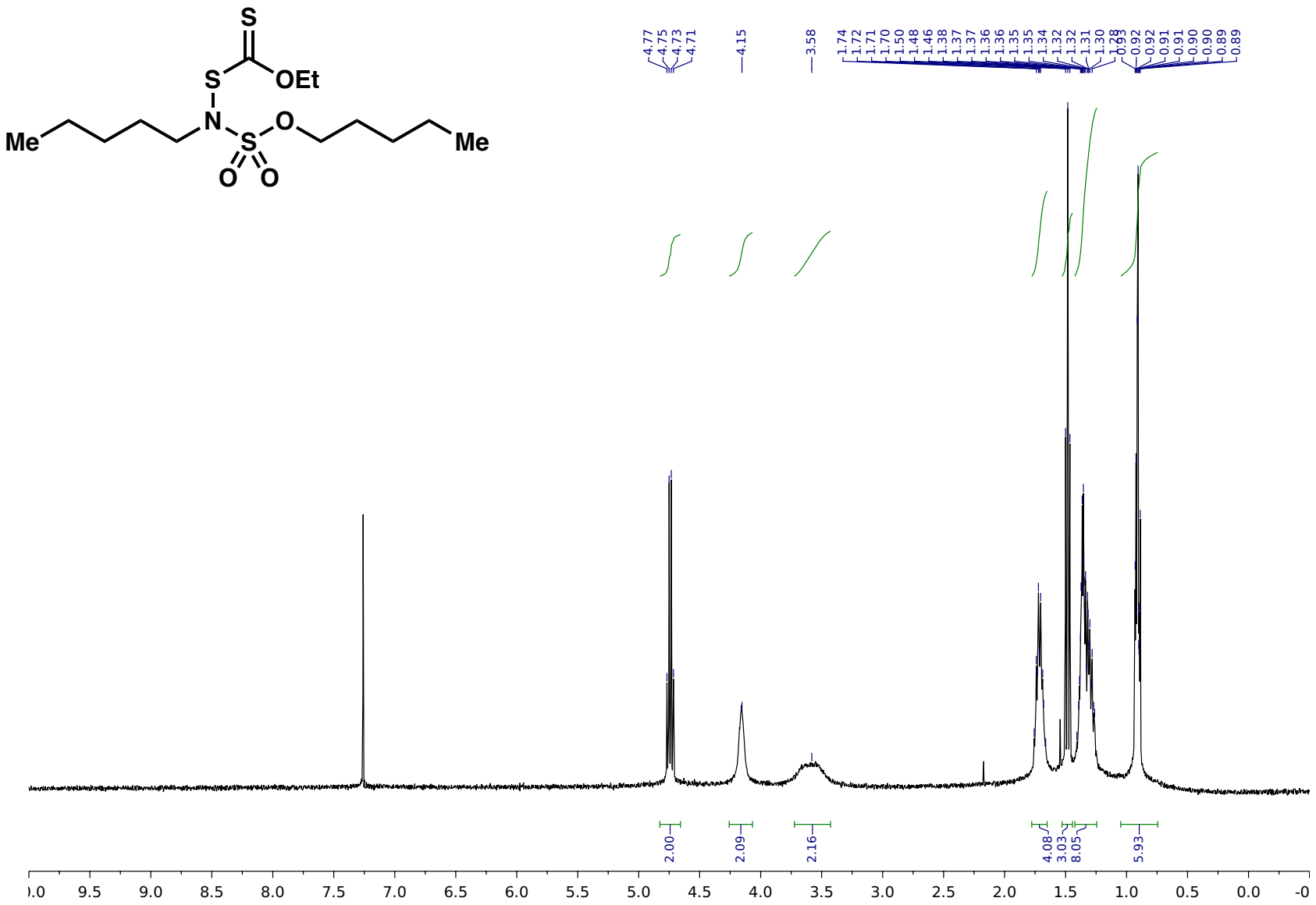
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for for pentyl 2-(pyridine-2-yl)propan-2-yl) ((ethoxycarbonothioyl)thio))sulfamate (**1e**)



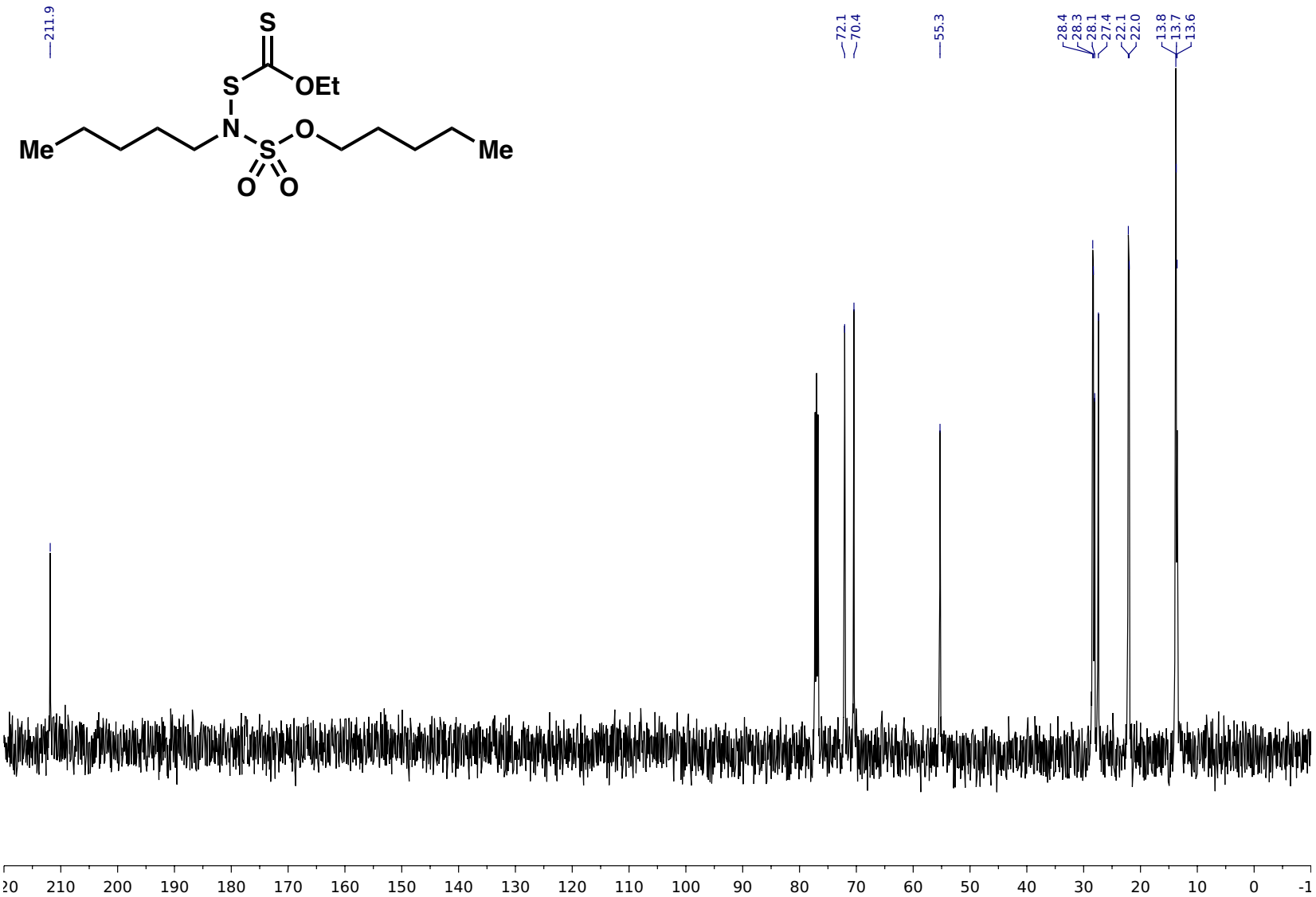
^{1}H NMR (400 MHz, $CDCl_3$) for pentyl cyclohexyl((ethoxycarbonothioyl)thio))sulfamate (**1f**)



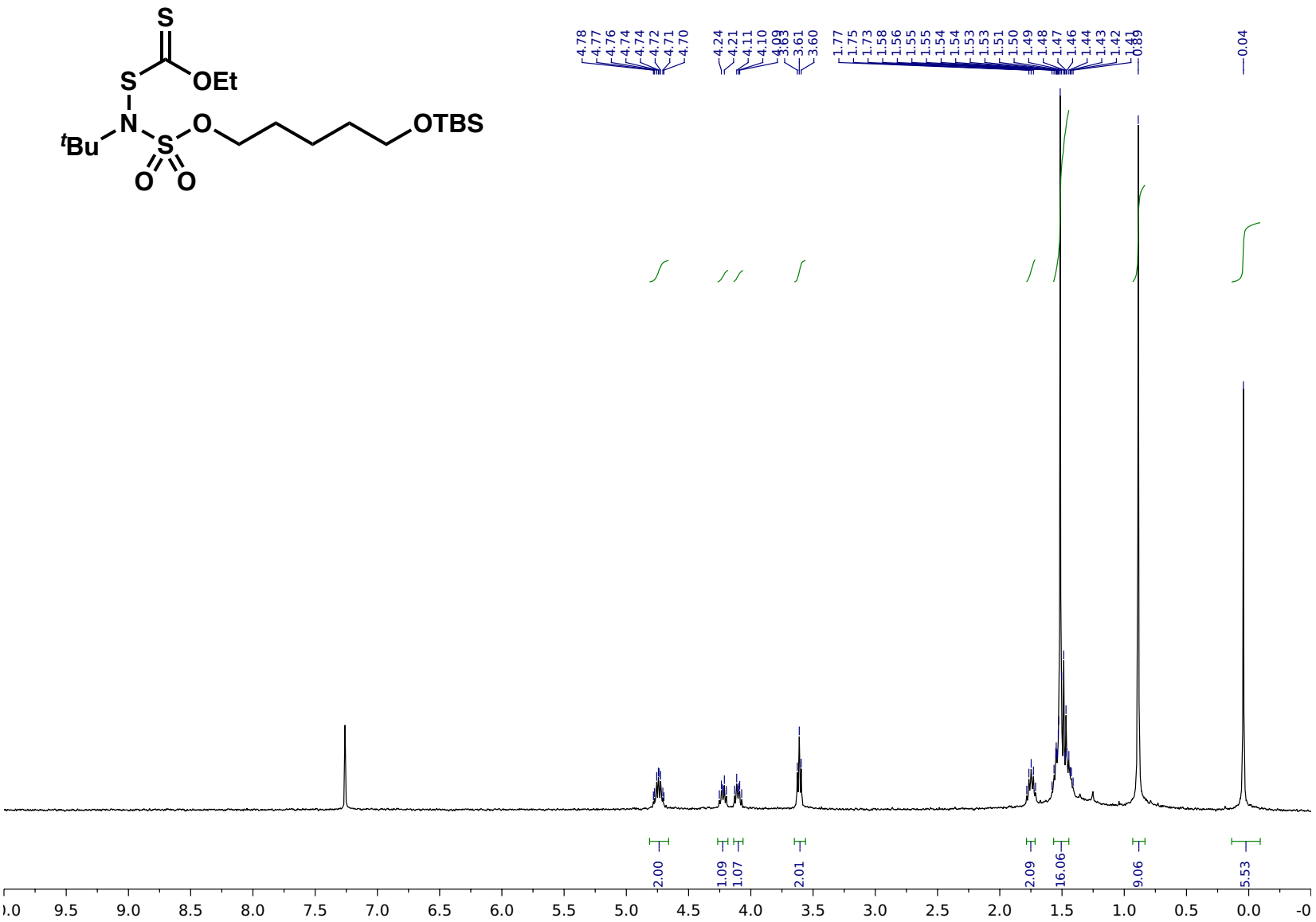
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for pentyl cyclohexyl((ethoxycarbonothioyl)thio))sulfamate (**1f**)



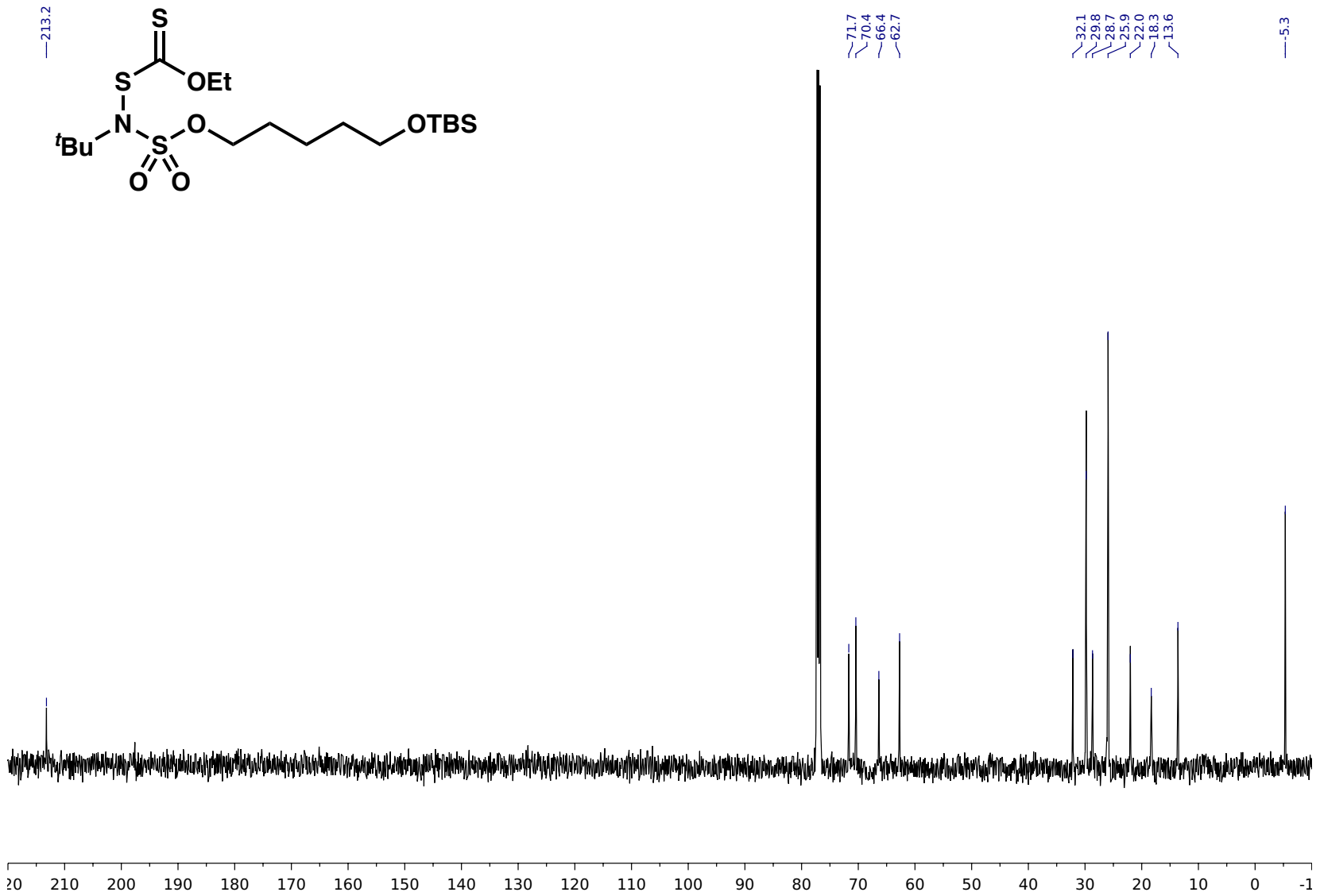
^{1}H NMR (400 MHz, $CDCl_3$) for pentyl pentyl((ethoxycarbonothioyl)thio))sulfamate (**1g**)



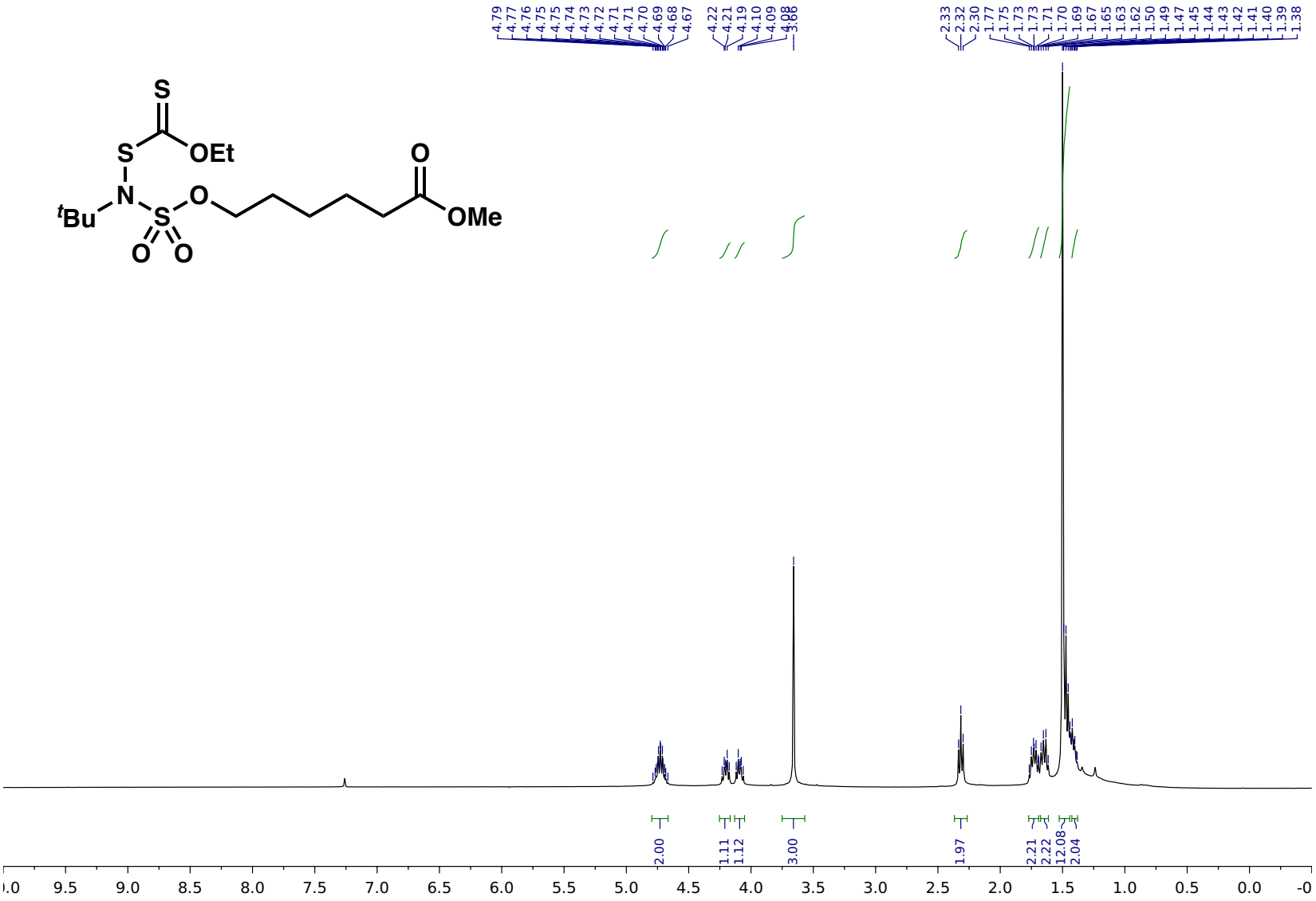
$^{13}C\{^{1}H\}$ NMR (126 MHz,$CDCl_3$) for pentyl pentyl((ethoxycarbonothioyl)thio))sulfamate (**1g**)



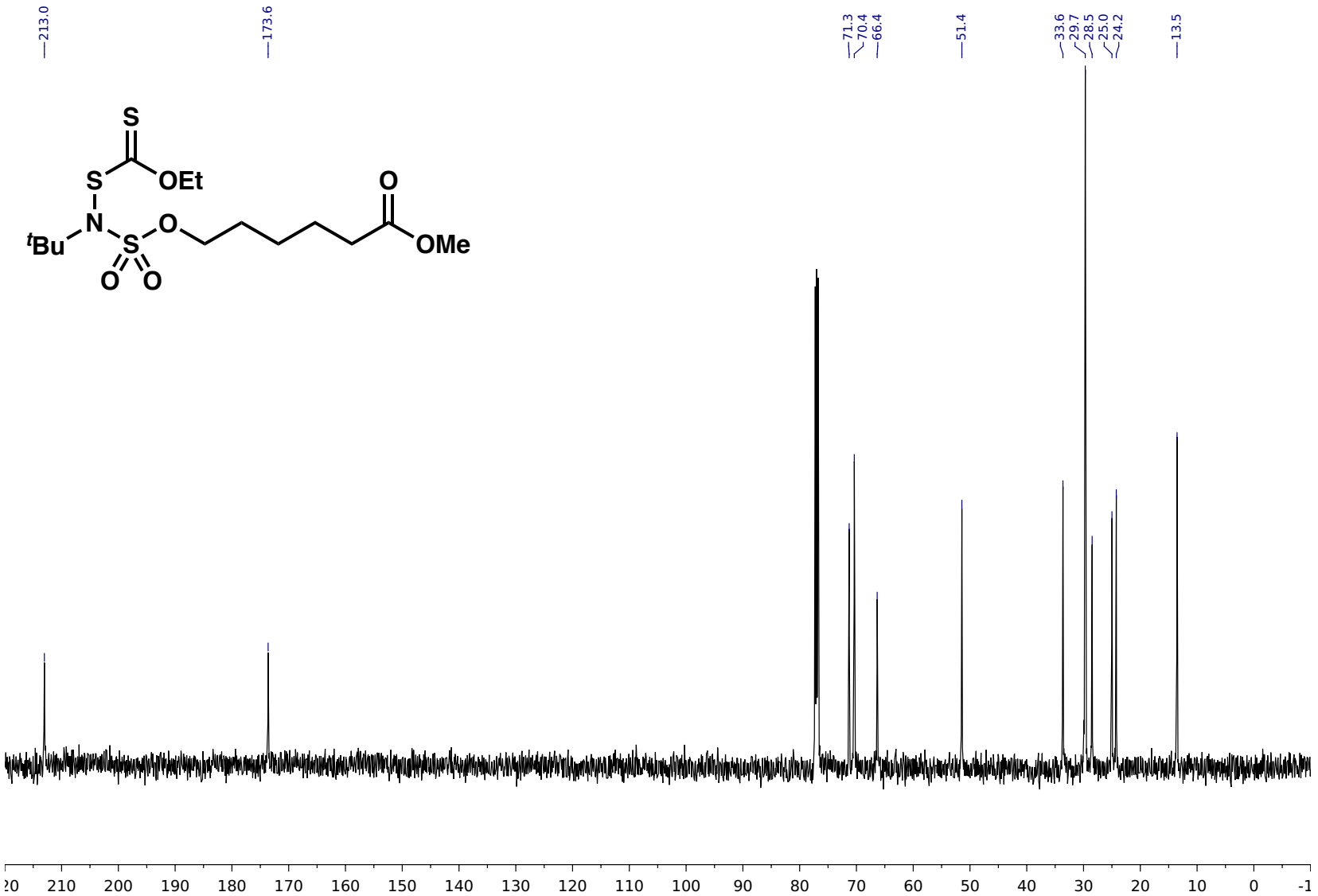
^{1}H NMR (400 MHz, $CDCl_3$) for 5-((*tert*-butyldimethylsilyl)oxy)pentyl *tert*-butyl((ethoxycarbonothioyl)thio))sulfamate (**1h**)



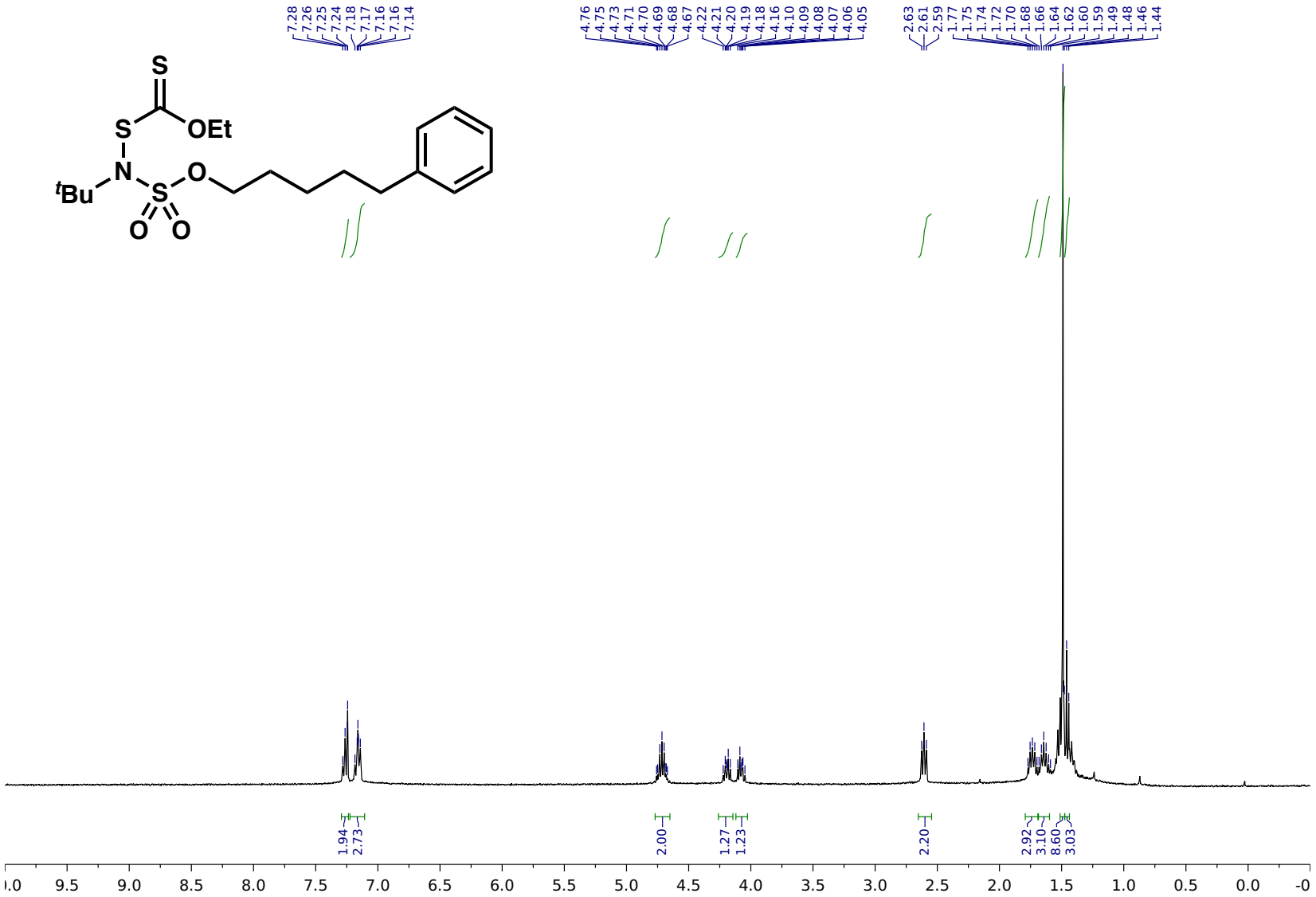
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 5-((*tert*-butyldimethylsilyl)oxy)pentyl *tert*-butyl((ethoxycarbonothioyl)thio))sulfamate (**1h**)



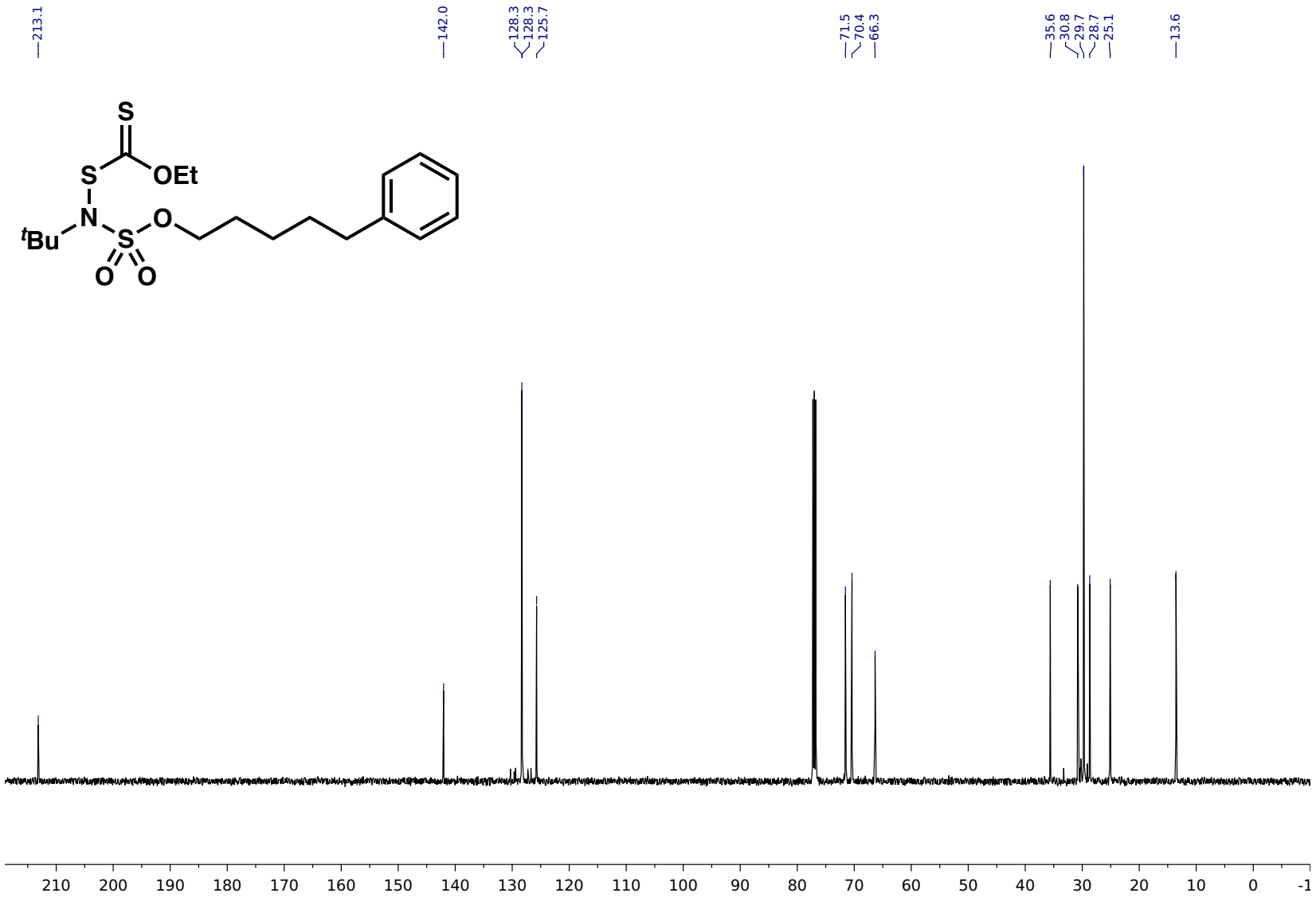
^{1}H NMR (400 MHz, $CDCl_3$) for (methyl 6-hydroxyhexanoate *tert*-butyl((ethoxycarbonothioyl)thio))sulfamate (**1i**)



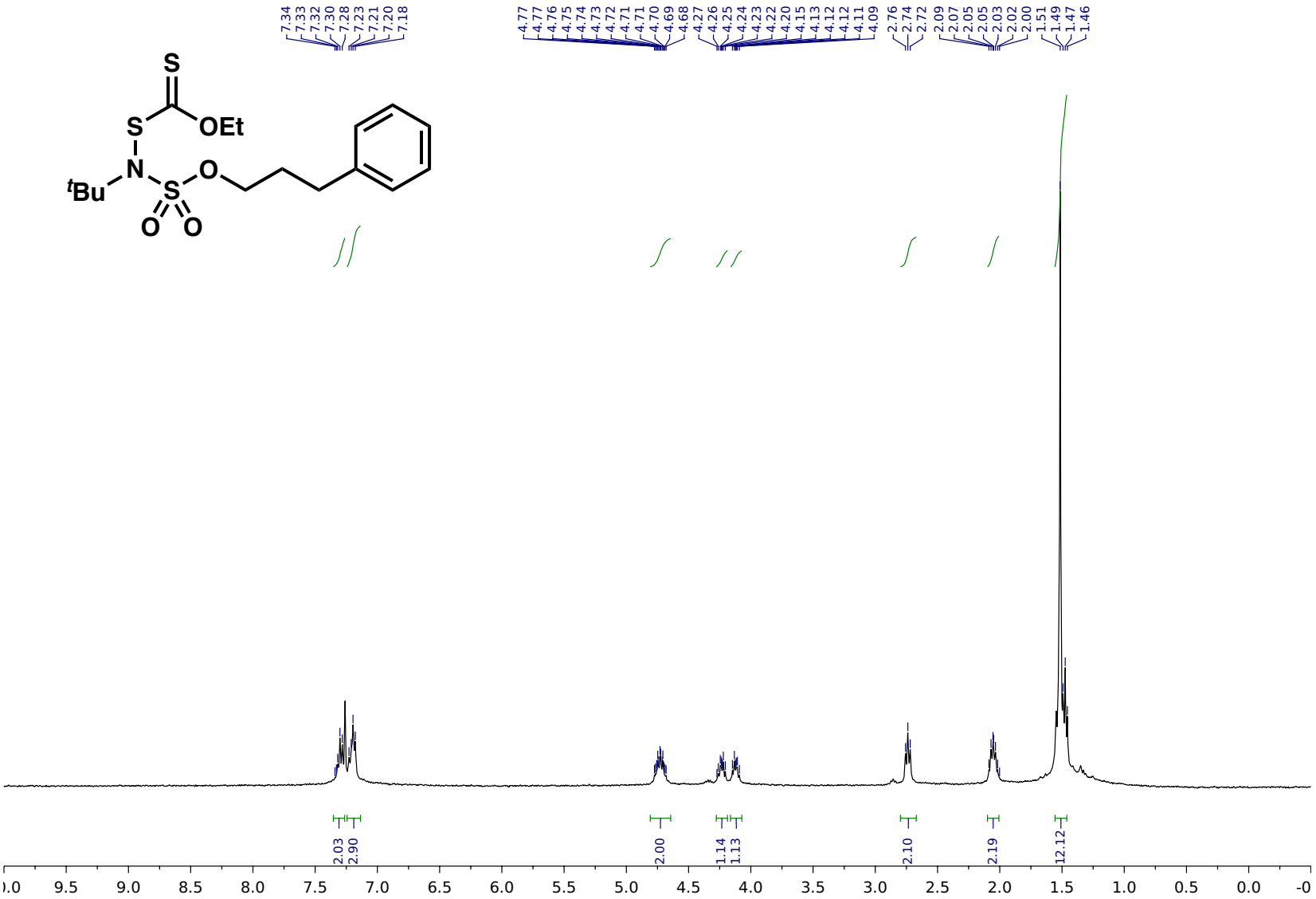
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for (methyl 6-hydroxyhexanoate *tert*-butyl((ethoxycarbonothioyl)thio))sulfamate (**1i**)



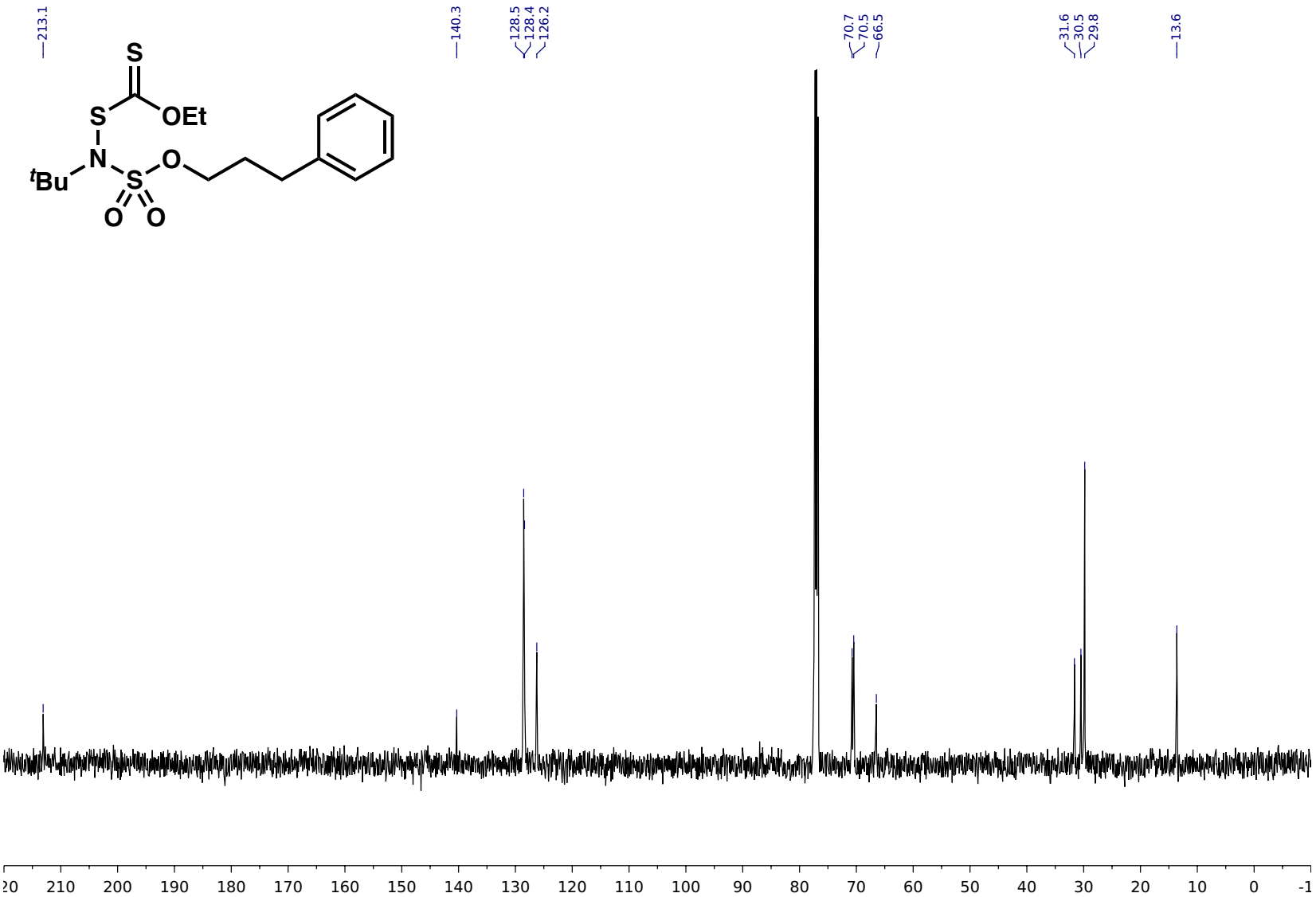
^{1}H NMR (400 MHz, $CDCl_3$) for 5-phenyl pentyl *tert*-butyl((ethoxycarbonothioyl)thio))sulfamate (**1j**)



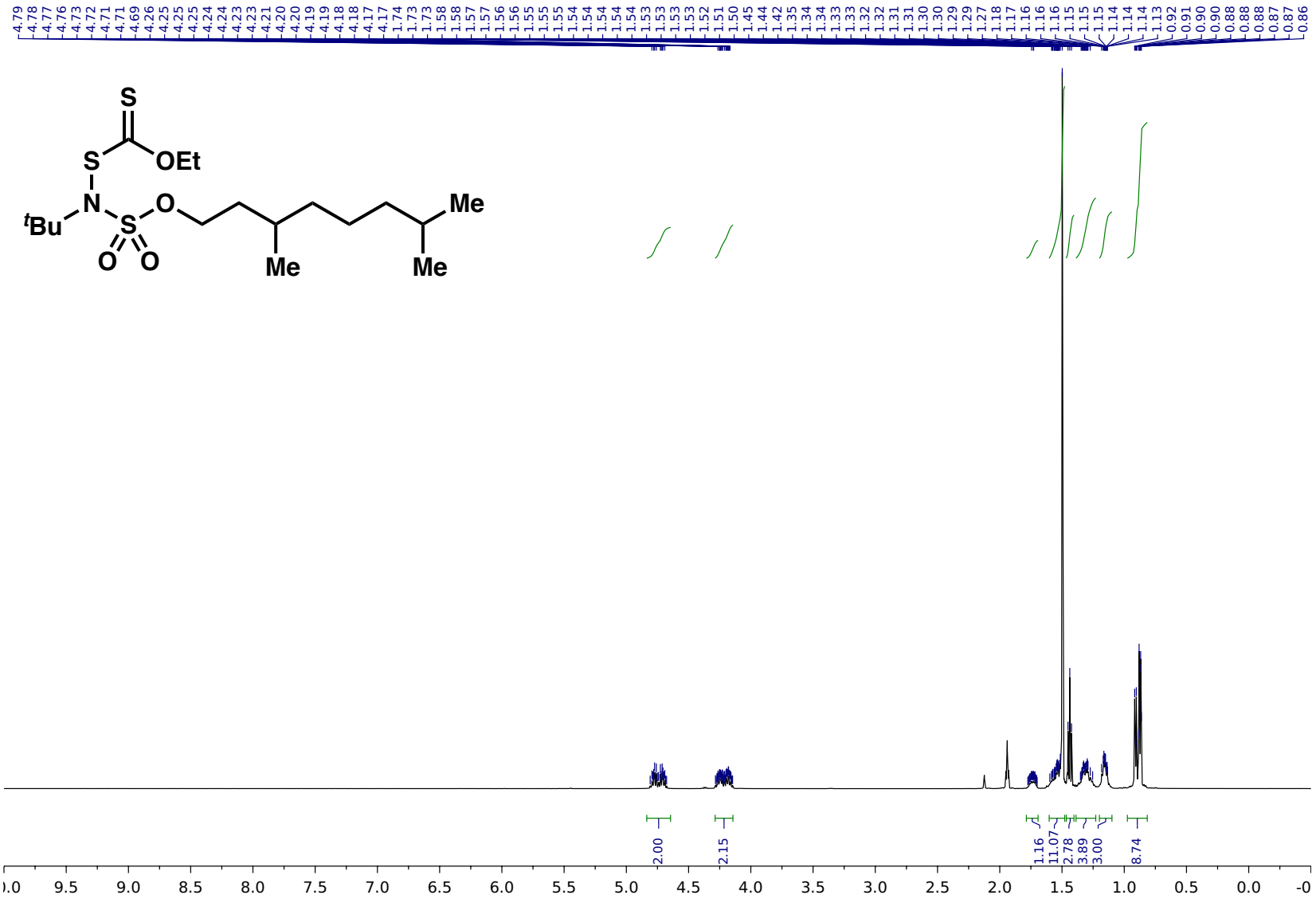
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 5-phenylpentyl *tert*-butyl((ethoxycarbonothioyl)thio))sulfamate (**1j**)



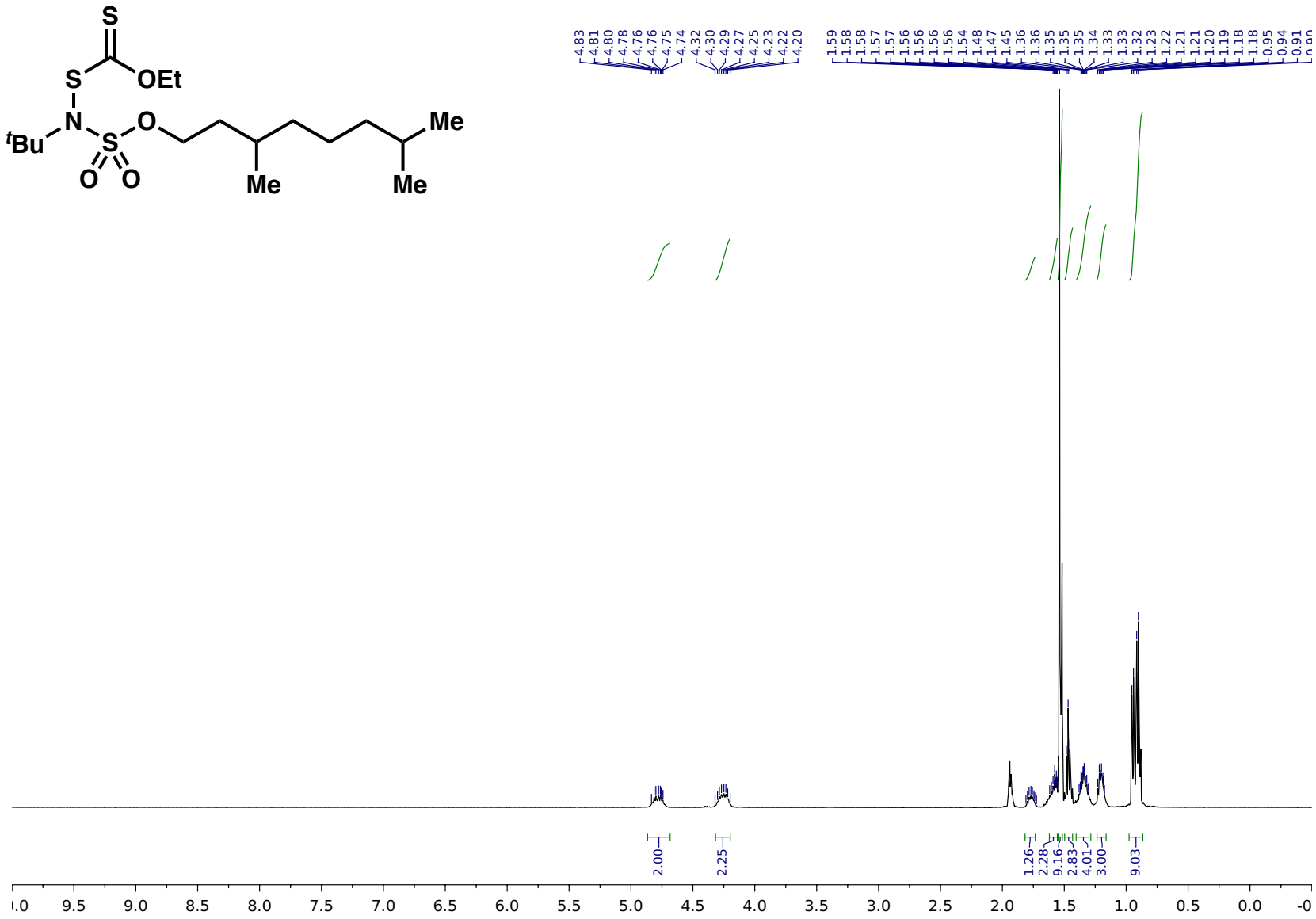
^{1}H NMR (400 MHz, $CDCl_3$) for (3-phenyl)propyl *tert*-butyl((ethoxycarbonothioyl)thio))sulfamate (**1k**)



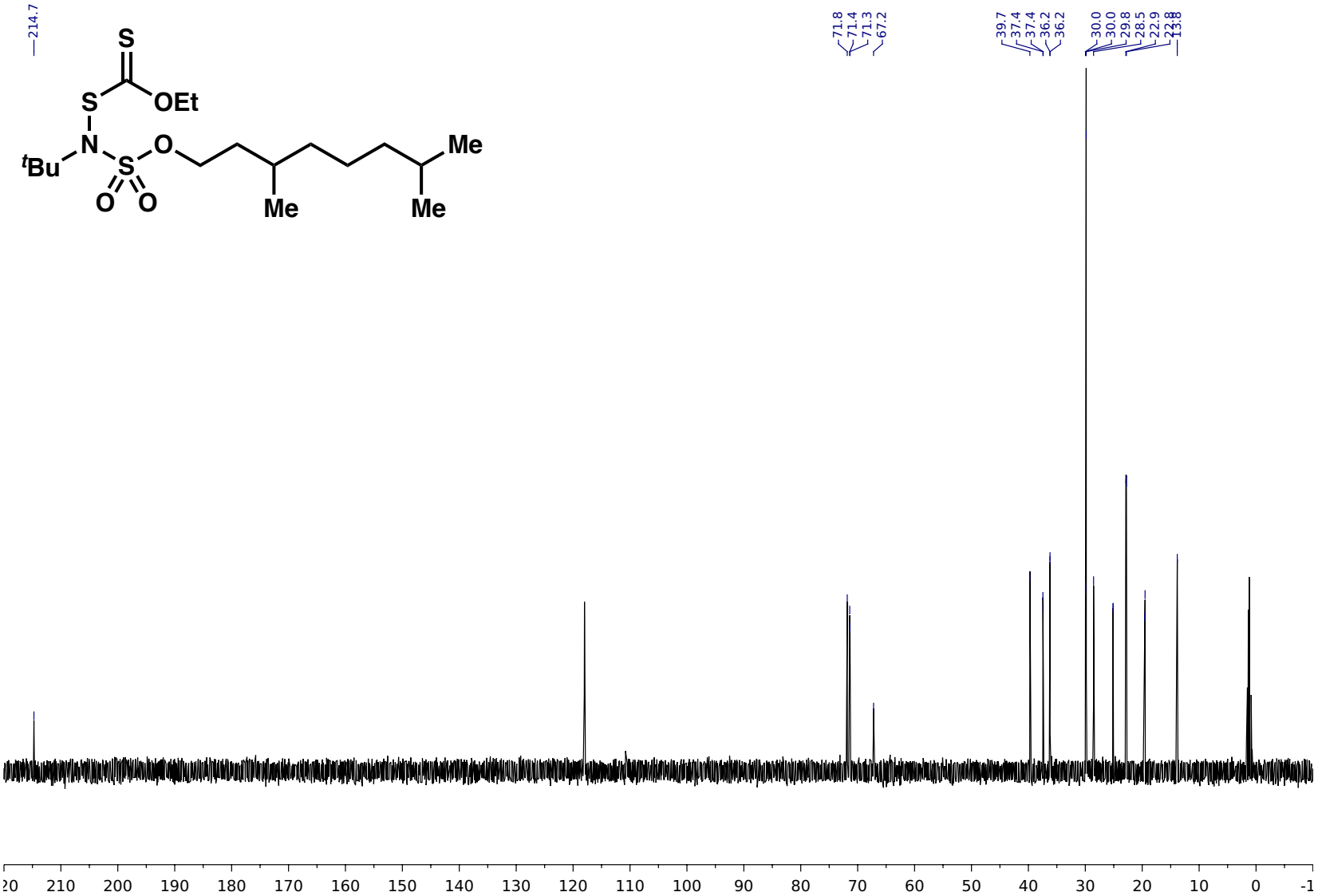
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for (3-phenyl)propyl *tert*-butyl((ethoxycarbonothioyl)thio))sulfamate (**1k**)



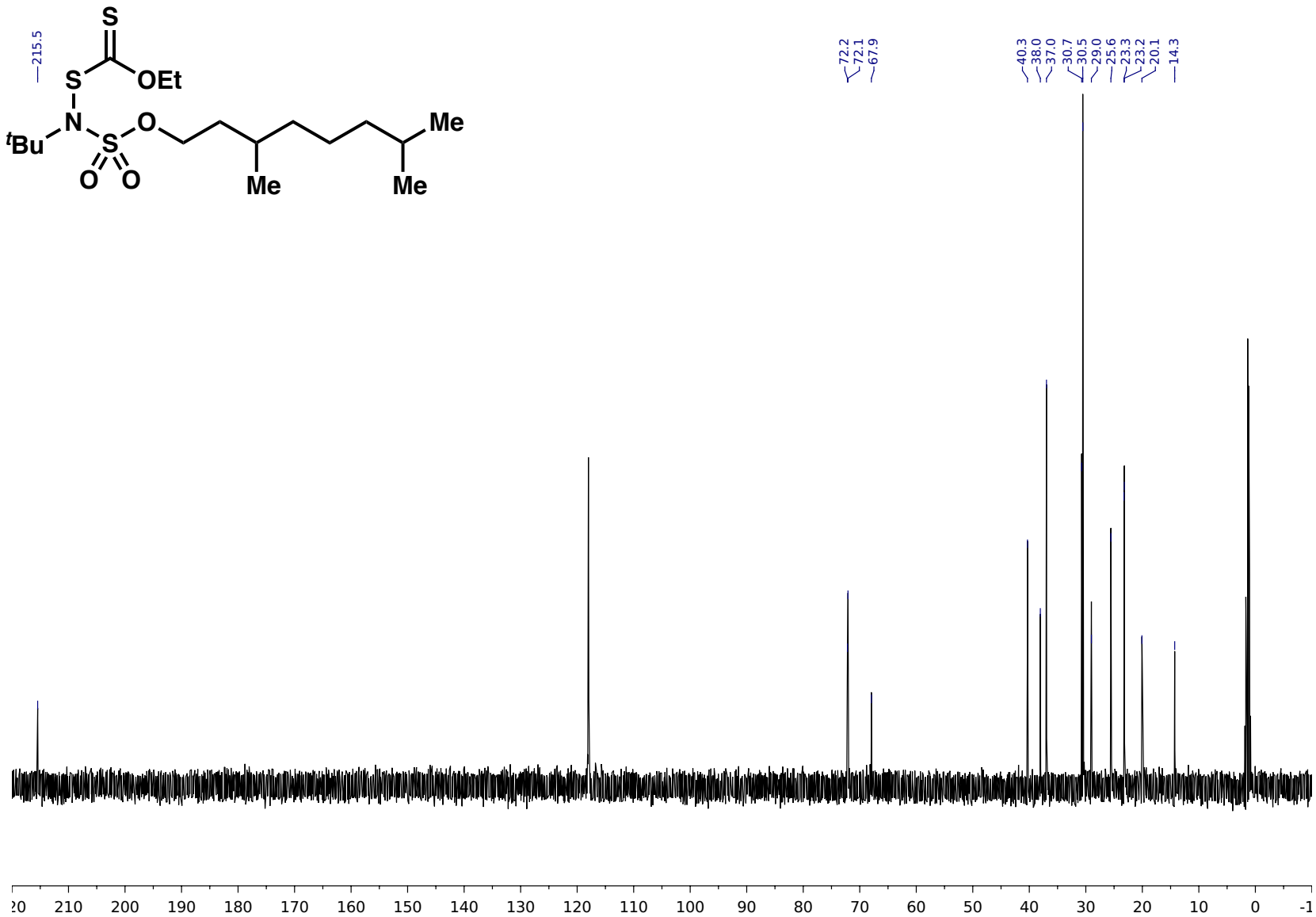
^{1}H NMR (500 MHz, CD_3CN, 25°C) for 3,7-dimethyloctyl *tert*- butyl((ethoxycarbonothioyl)thio))sulfamate (**1l**)



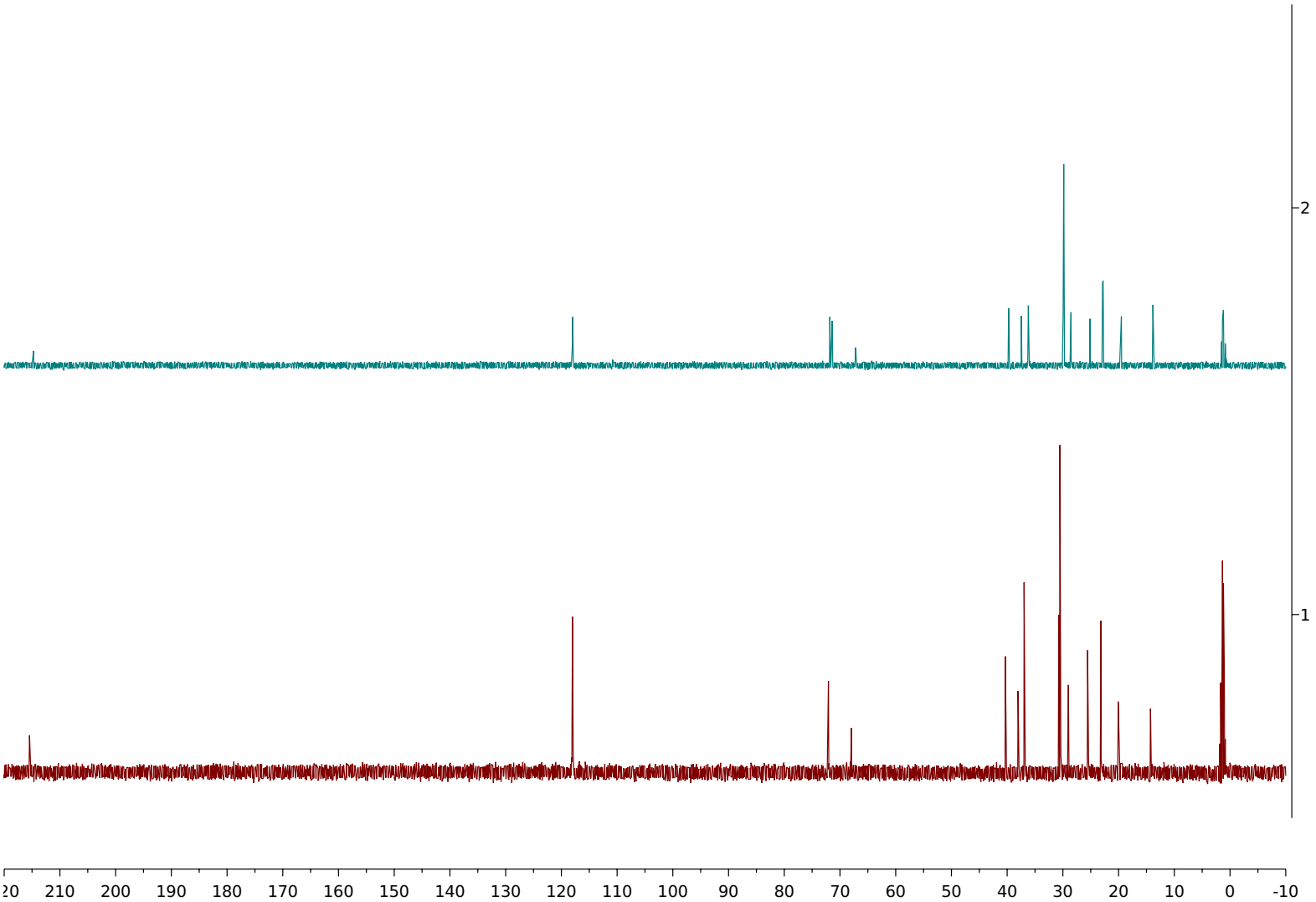
^{1}H NMR (500 MHz, CD_3CN, 80°C) for 3,7-dimethyloctyl *tert*- butyl((ethoxycarbonothioyl)thio))sulfamate (**1l**)



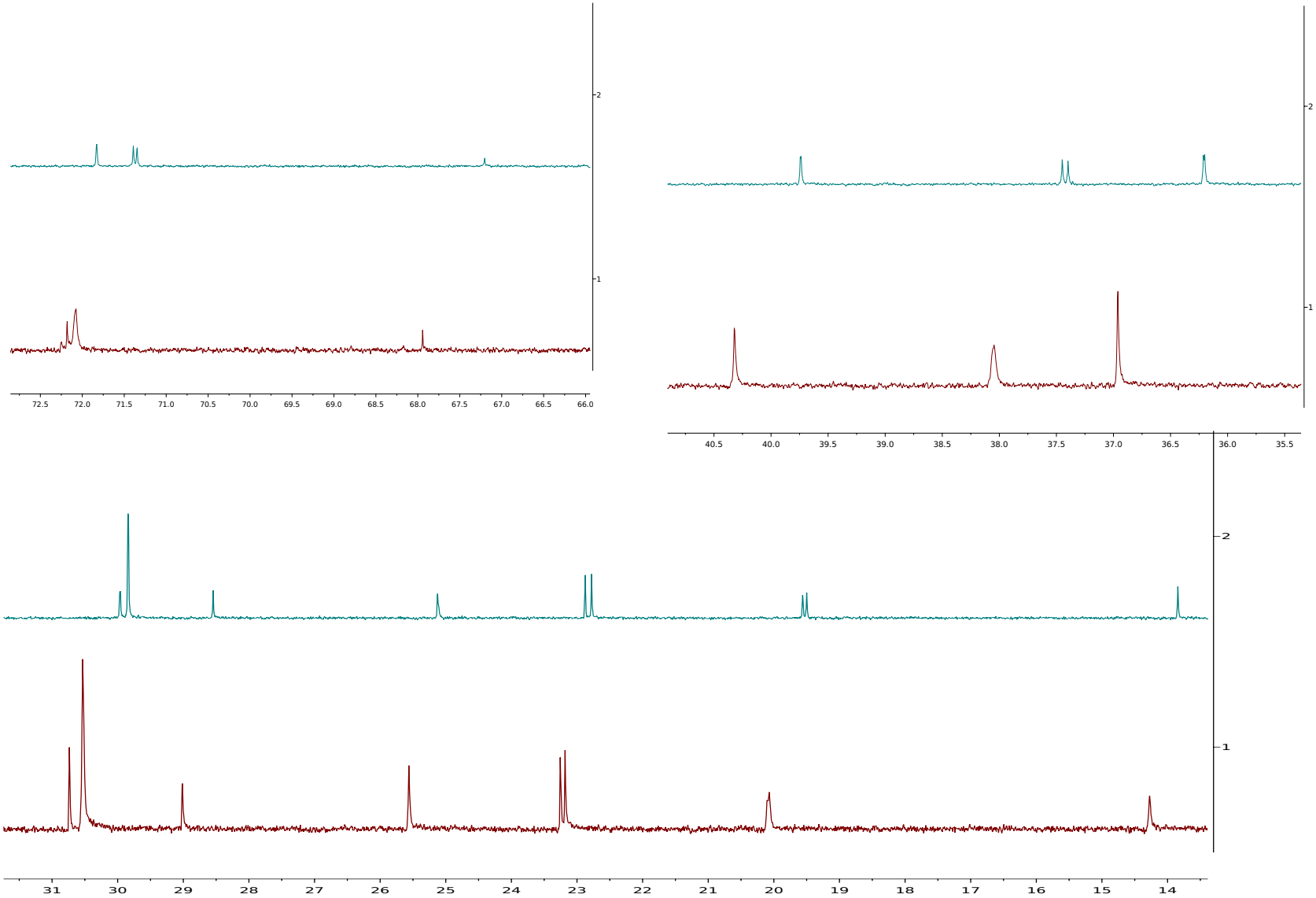
$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3CN, 25°C) for 3,7-dimethyloctyl *tert*- butyl((ethoxycarbonothioyl)thio))sulfamate (**1l**)



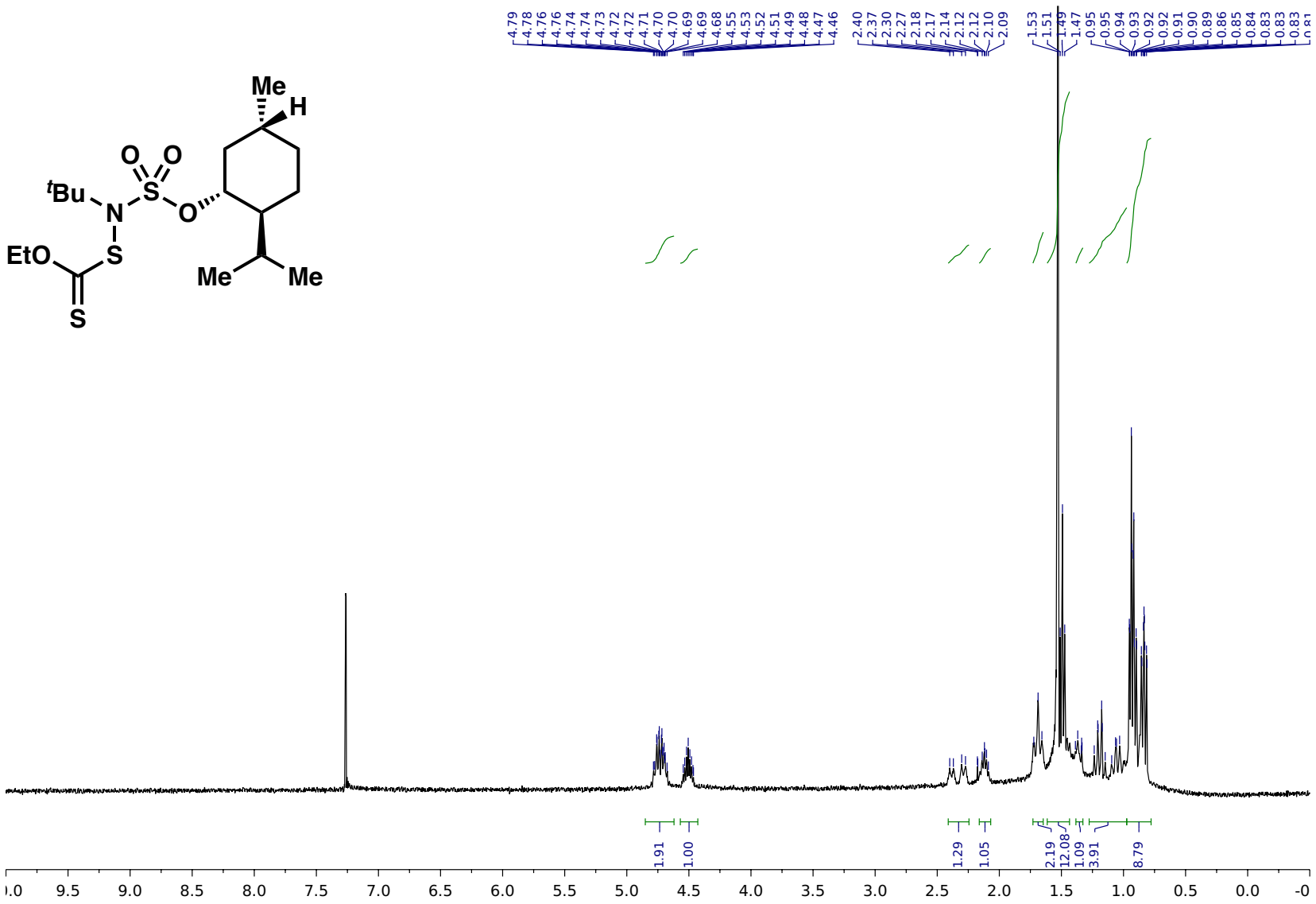
$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3CN, 80°C) for 3,7-dimethyloctyl *tert*- butyl((ethoxycarbonothioyl)thio))sulfamate (**1l**)



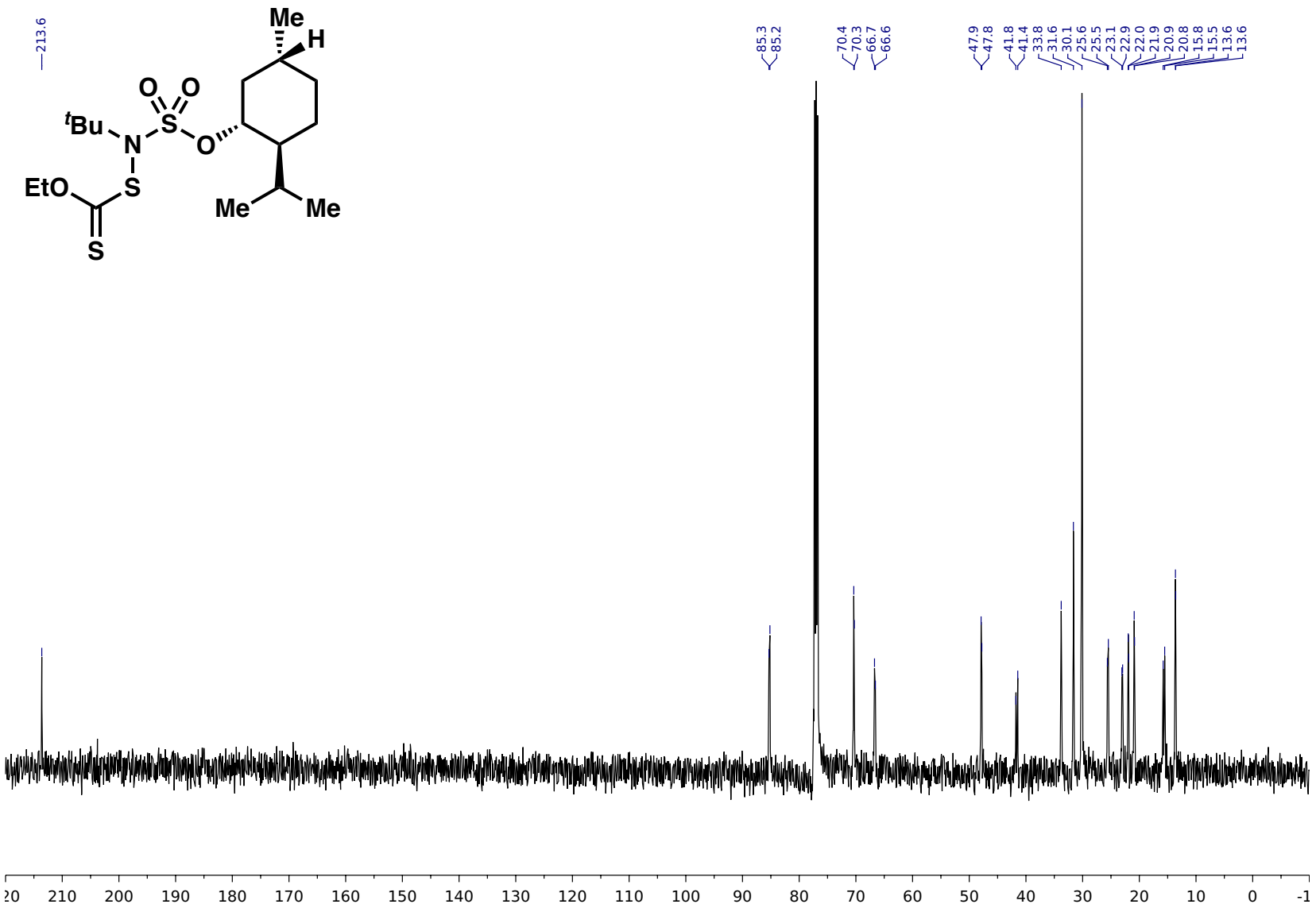
$^{13}C\{^{1}H\}$ NMR stacked for **1l** [Top: @ 25 °C Vs. Bottom: @ 80 °C]



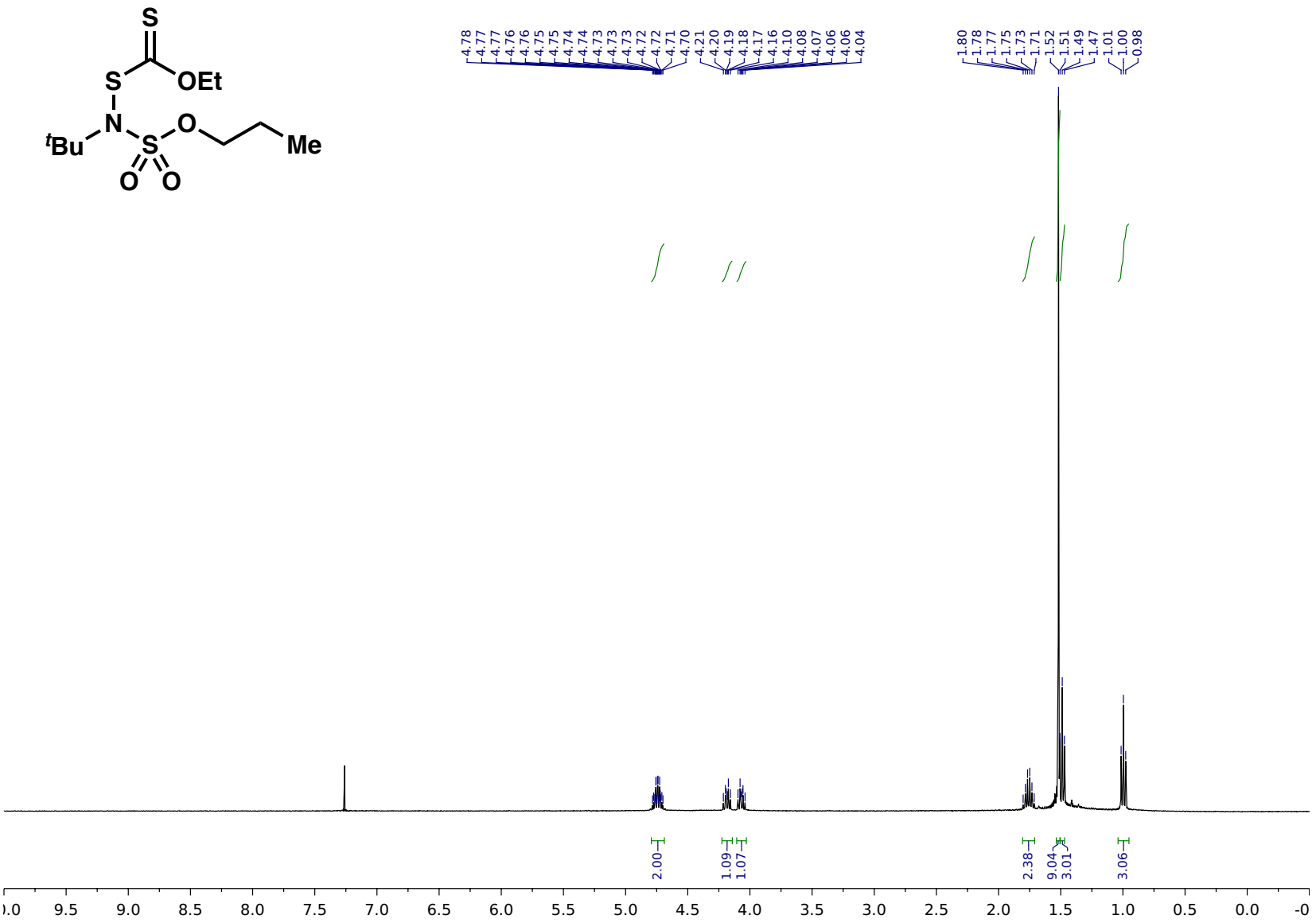
Expanded $^{13}C\{^{1}H\}$ NMR stacked for **1l** [Top: @ 25 °C Vs. Bottom: @ 80 °C]



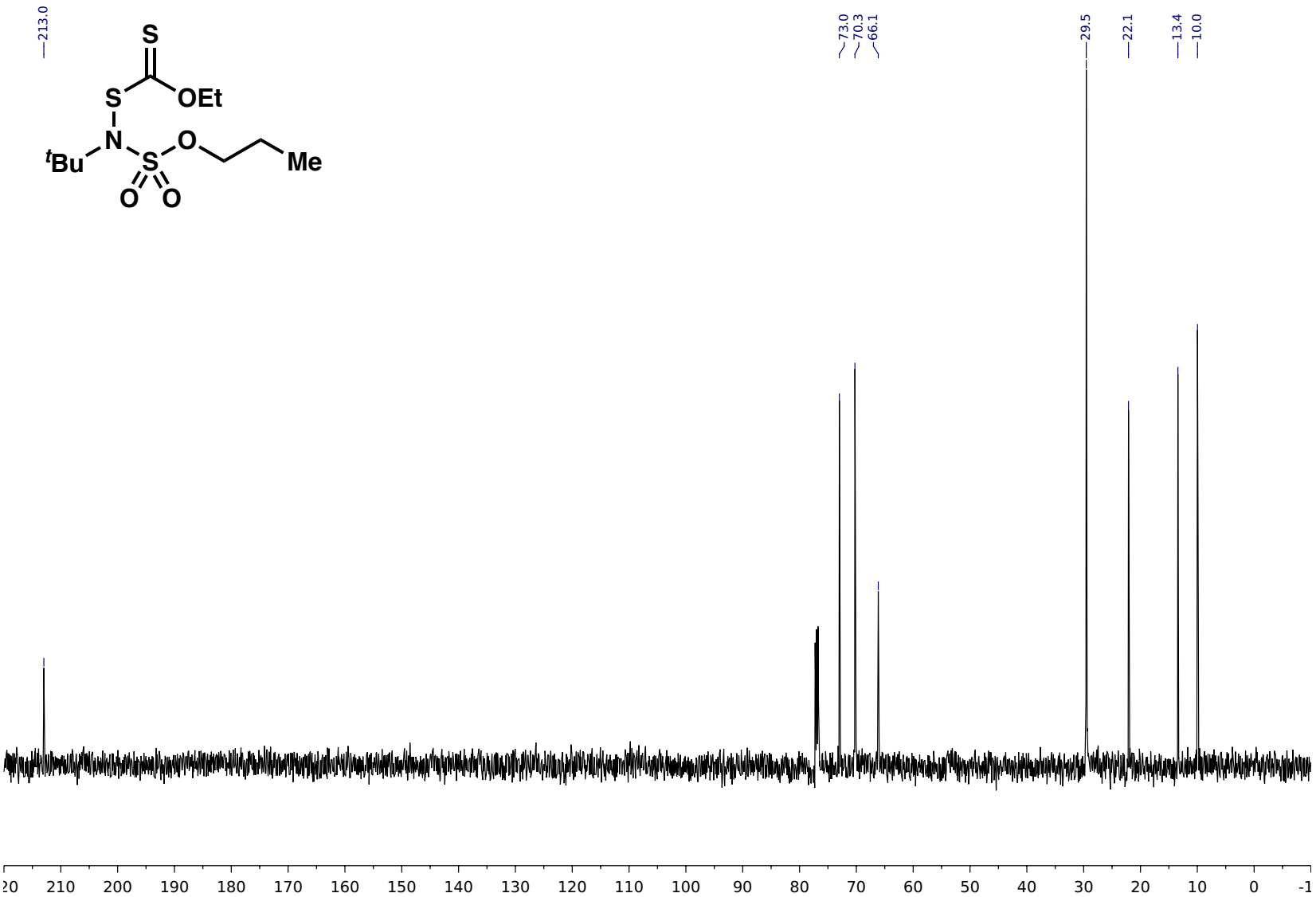
^{1}H NMR (400 MHz, $CDCl_3$) for (1*R*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl *tert*-butyl((ethoxycarbonothioyl)thio)sulfamate (**1m**)



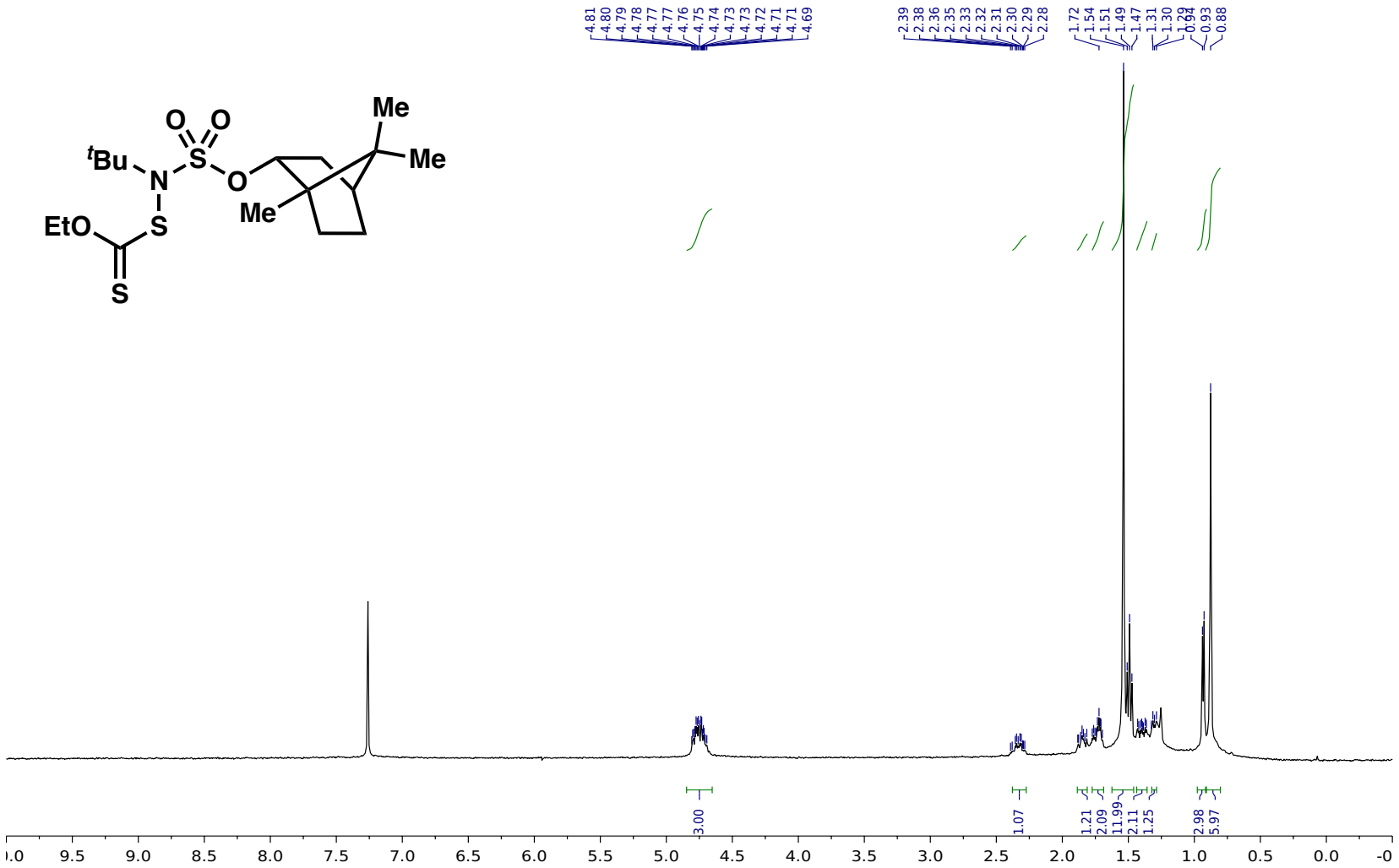
$^{13}C\{^{1}H\}$NMR(126 MHz,$CDCl_3$) for (1*R*, 2*S*, 5*R*)-2-isopropyl-5-methylcyclohexyl*tert*-butyl((ethoxycarbonothioyl)thio)sulfamate (**1m**)



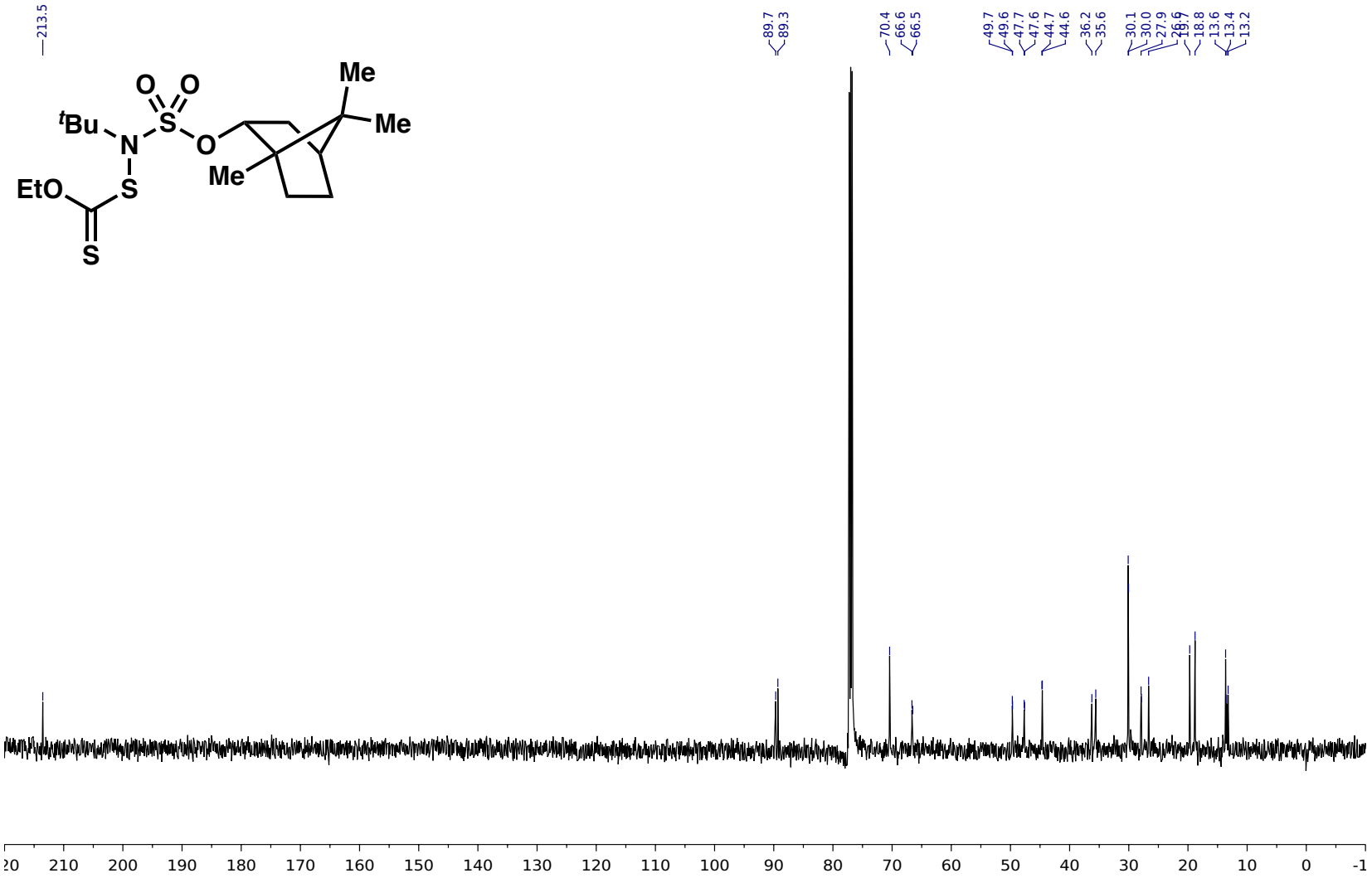
^{1}H NMR (400 MHz, $CDCl_3$) for propyl *tert*-butyl((ethoxycarbonothioyl)thio)sulfamate (**1n**)



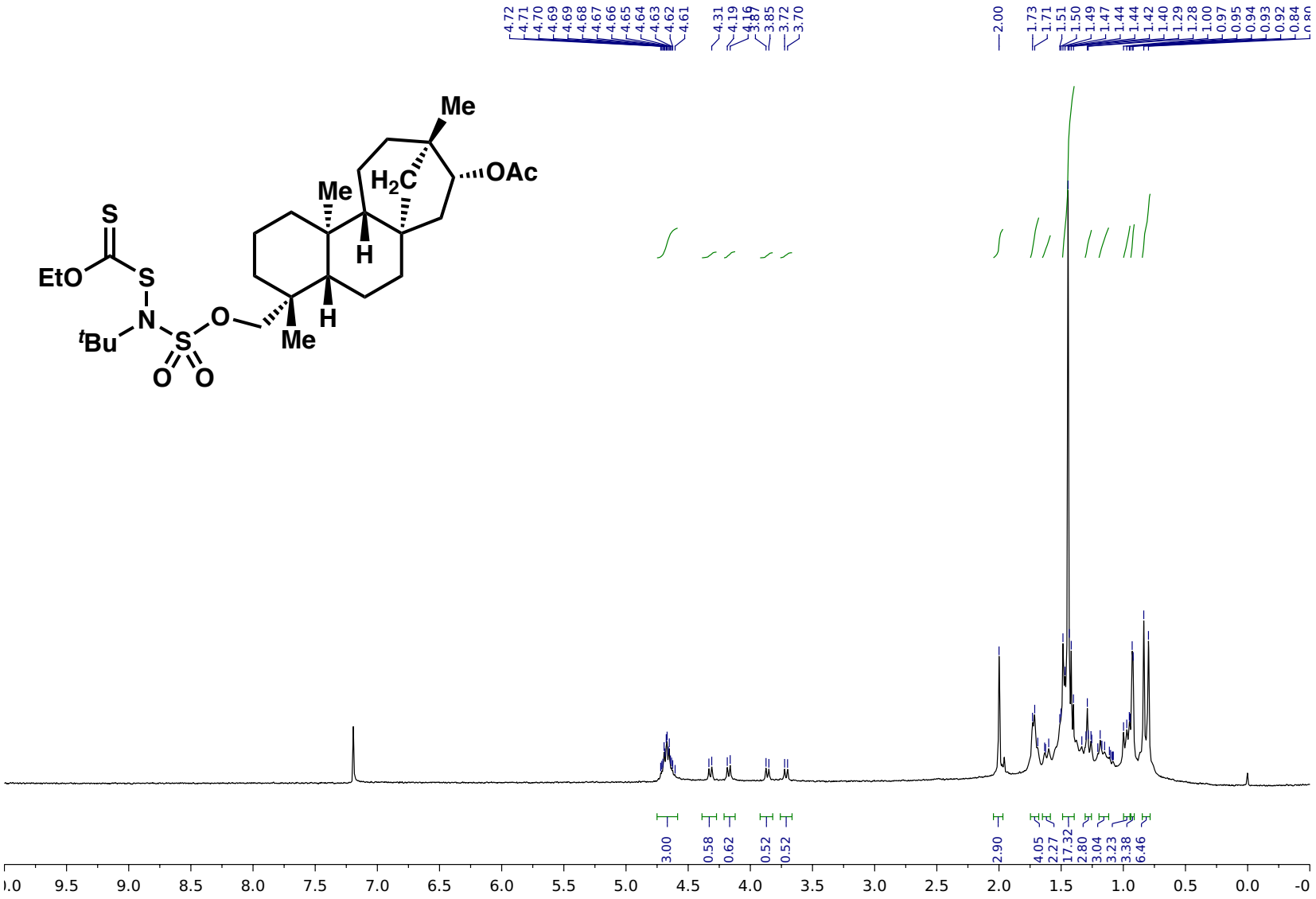
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for propyl *tert*-butyl((ethoxycarbonothioyl)thio)sulfamate (**1n**)



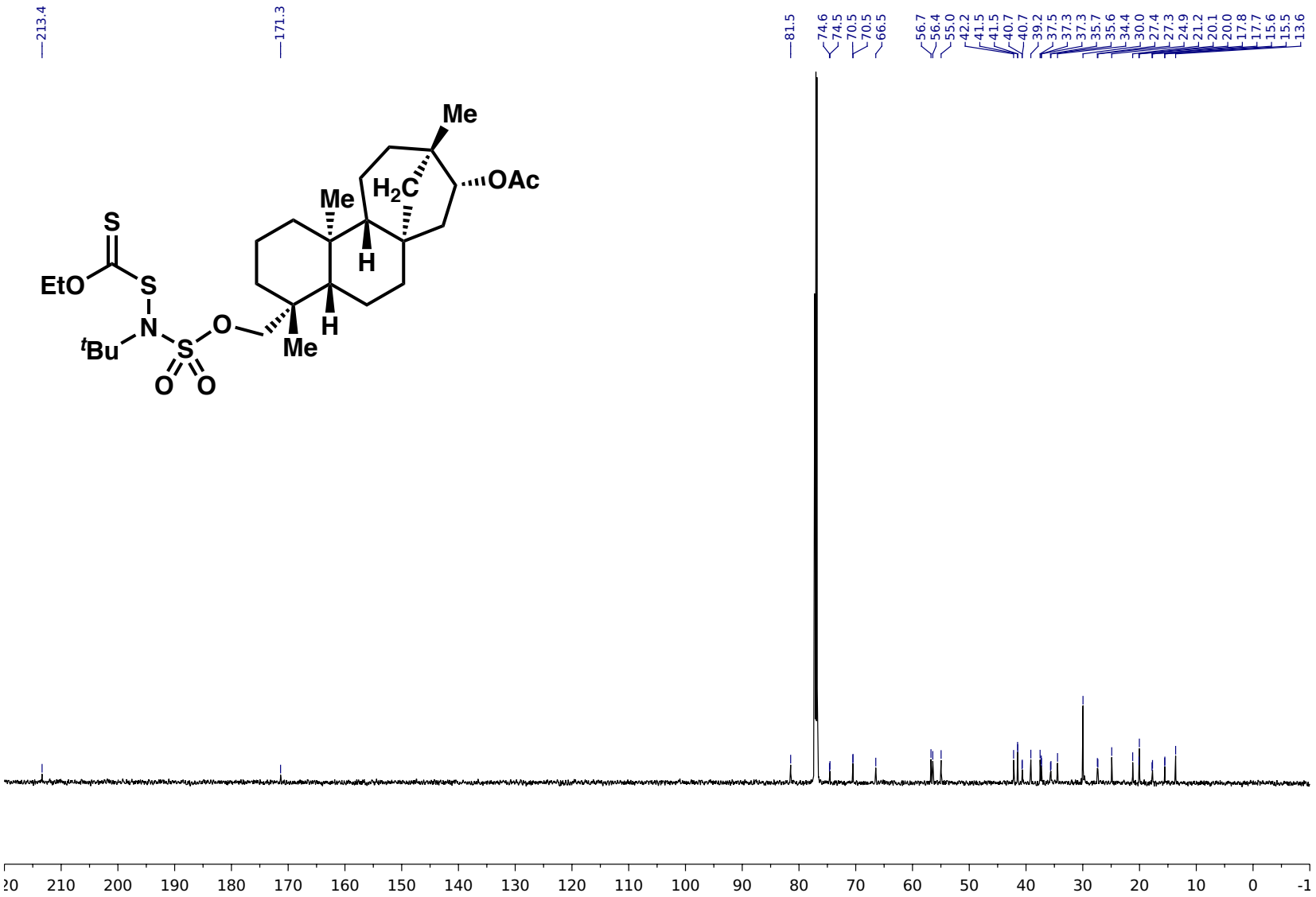
^{1}H NMR (400 MHz, $CDCl_3$) for (1*R*, 2*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl *tert*-butyl((ethoxycarbonothioyl)thio)sulfamate (**1o**)



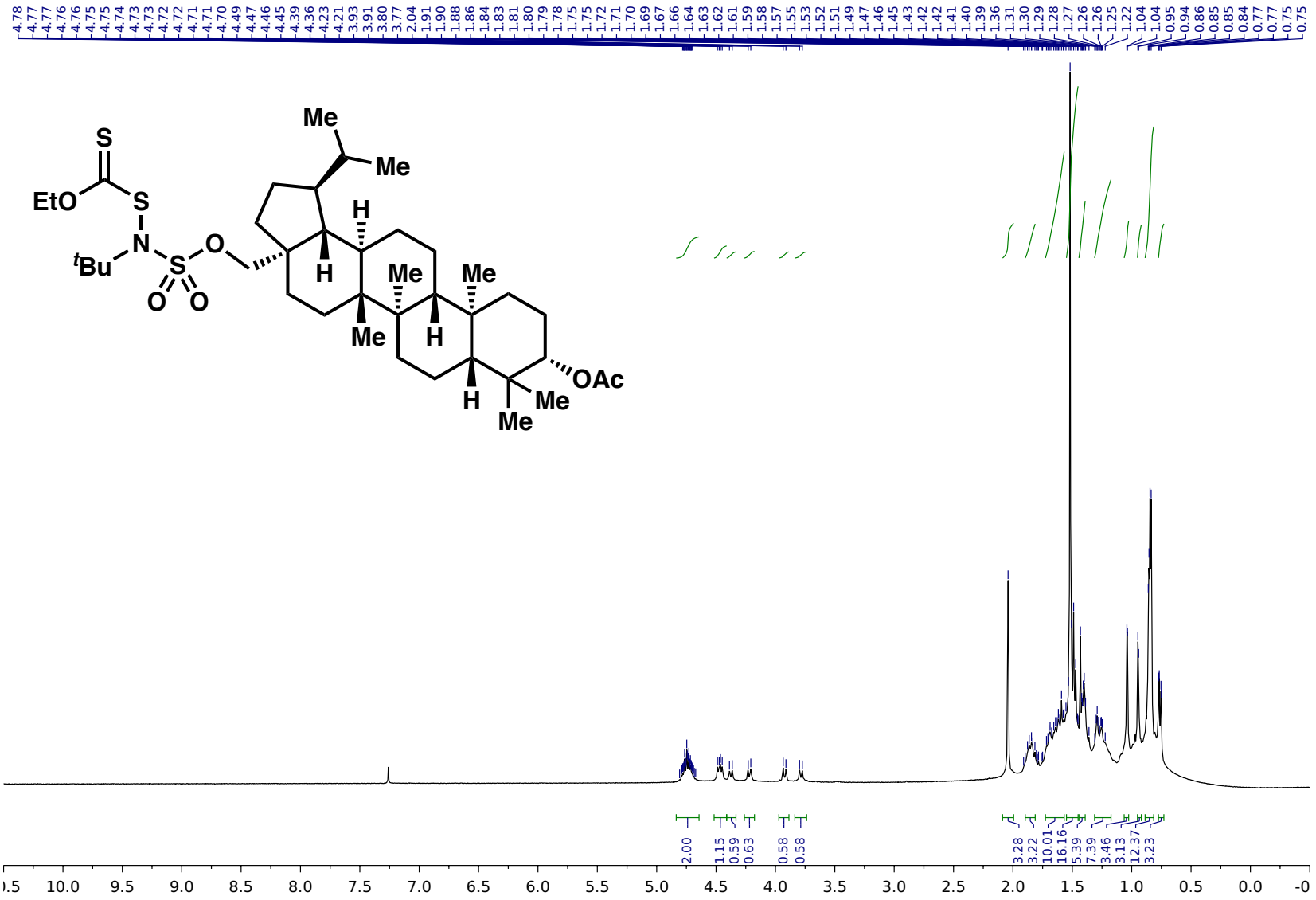
$^{13}C\{^{1}H\}$ NMR (126 MHz ,$CDCl_3$) for (1*R*, 2*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl *tert*-butyl((ethoxycarbonothioyl)thio) sulfamate (**1o**)



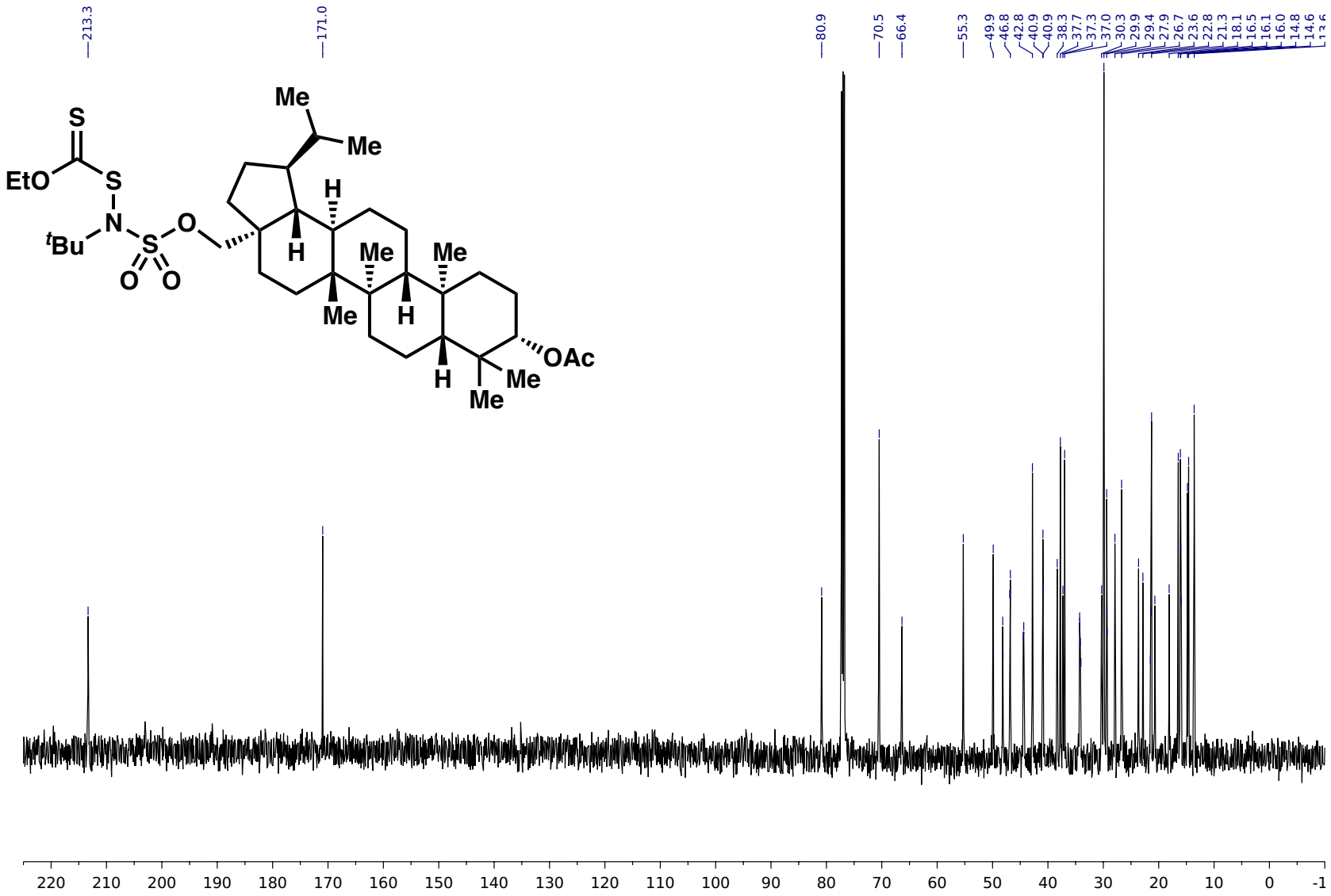
^{1}H NMR (400 MHz, $CDCl_3$) for (–)-16-acetoxy-13-methyl-17-norkaurane *tert*-butyl((ethoxycarbonothioyl)thio) sulfamate (**1p**)



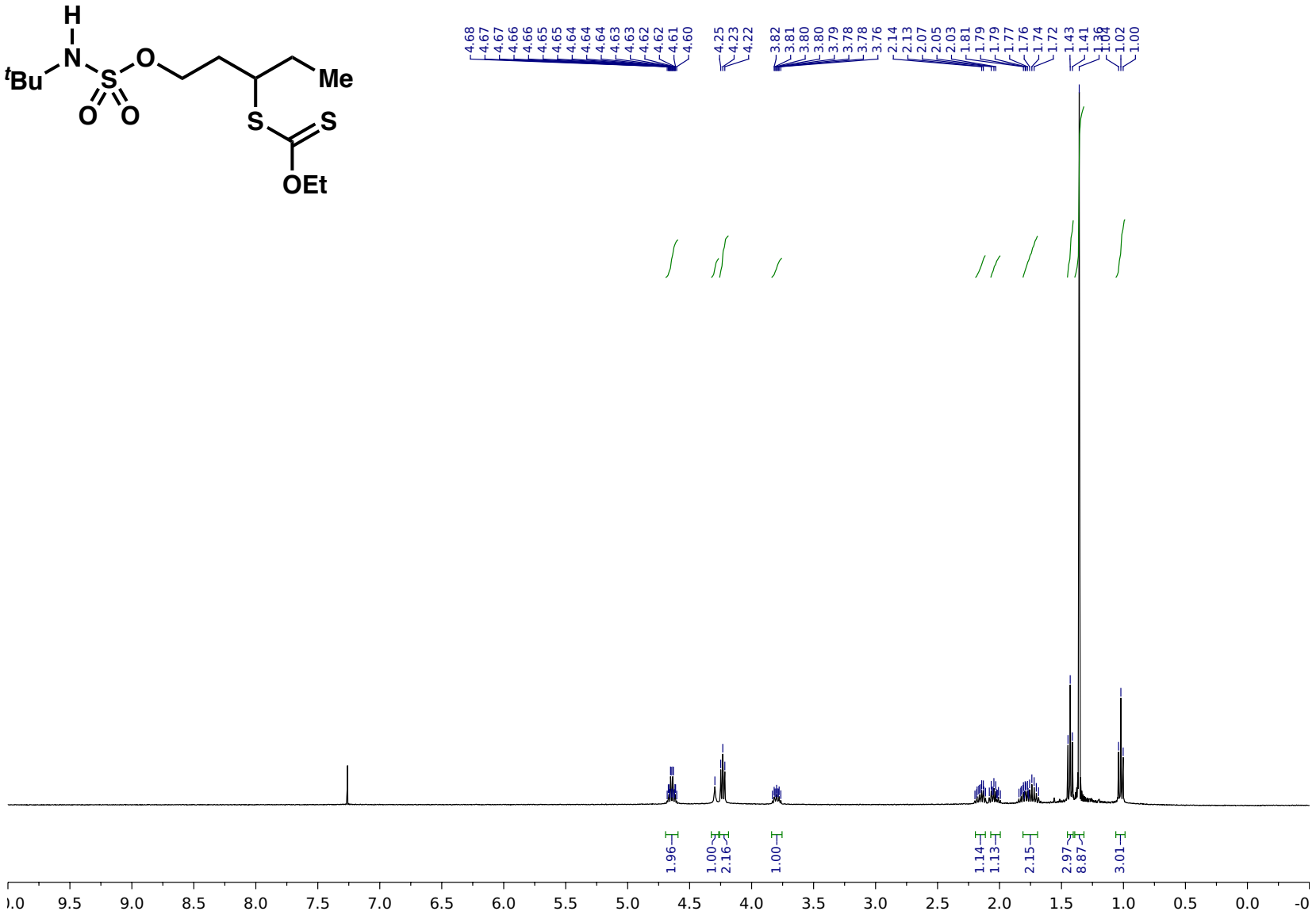
$^{13}C\{^{1}H\}$ NMR (176 MHz, $CDCl_3$) for (–)-16-acetoyxy-13-methyl-17-norkaurane *tert*-butyl((ethoxycarbonothioyl)thio) sulfamate (**1p**)



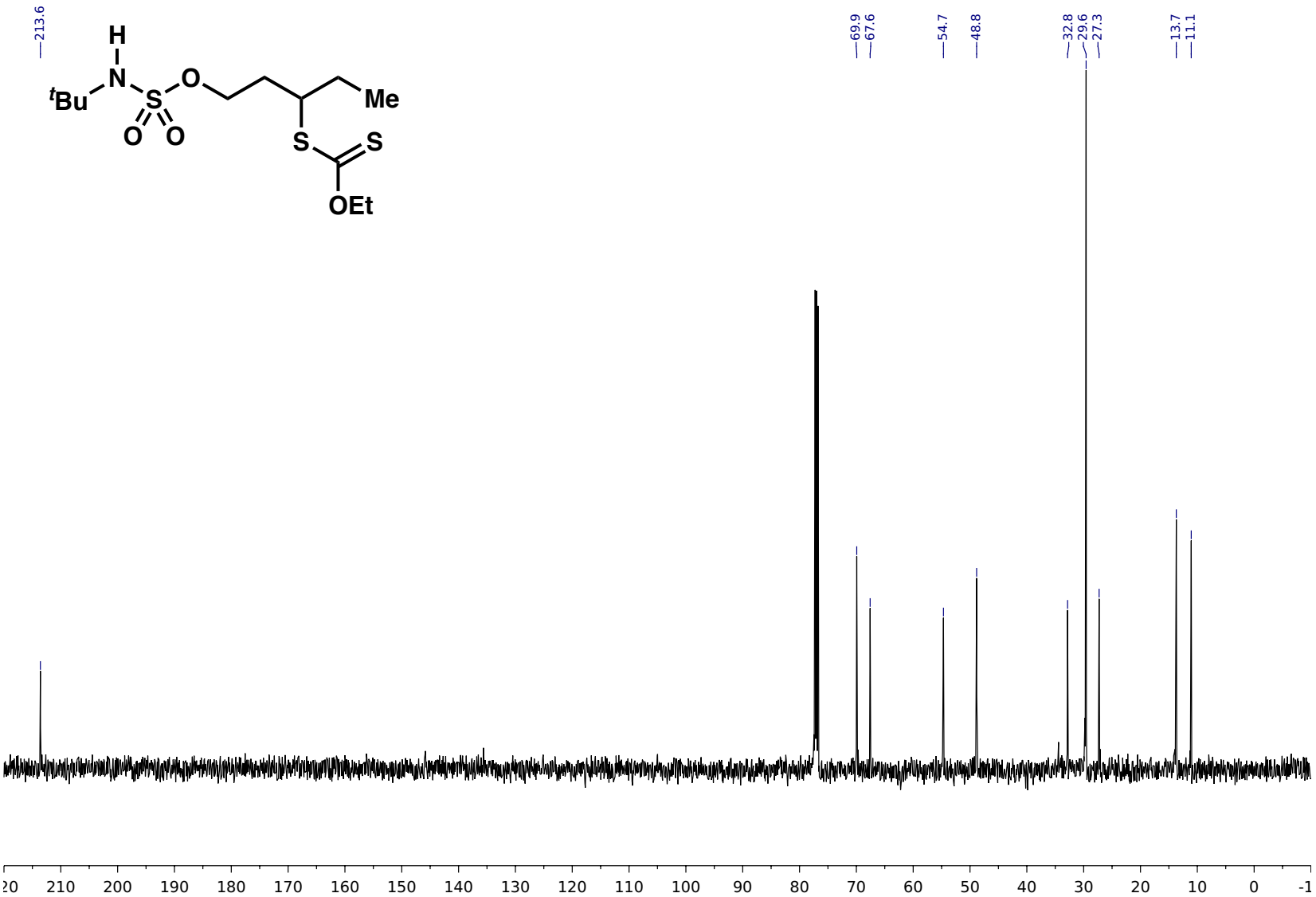
^{1}H NMR (400 MHz, $CDCl_3$) for 3-acetoxydihydrobetulinic *tert*-butyl((ethoxycarbonothioyl)thio) sulfamate (**1q**)



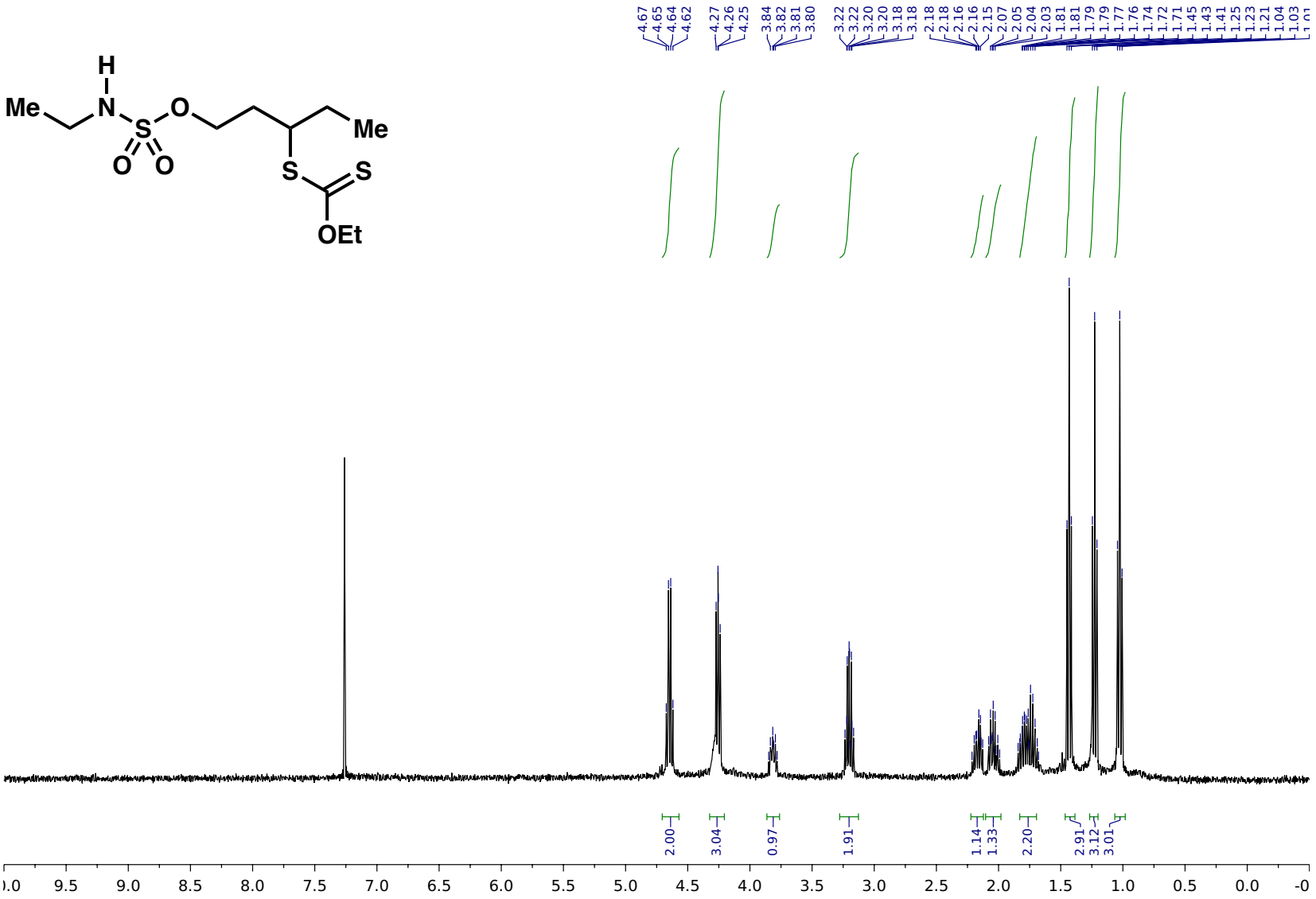
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-acetoxydihydrobetulinic *tert*-butyl((ethoxycarbonothioyl)thio) sulfamate (**1q**)



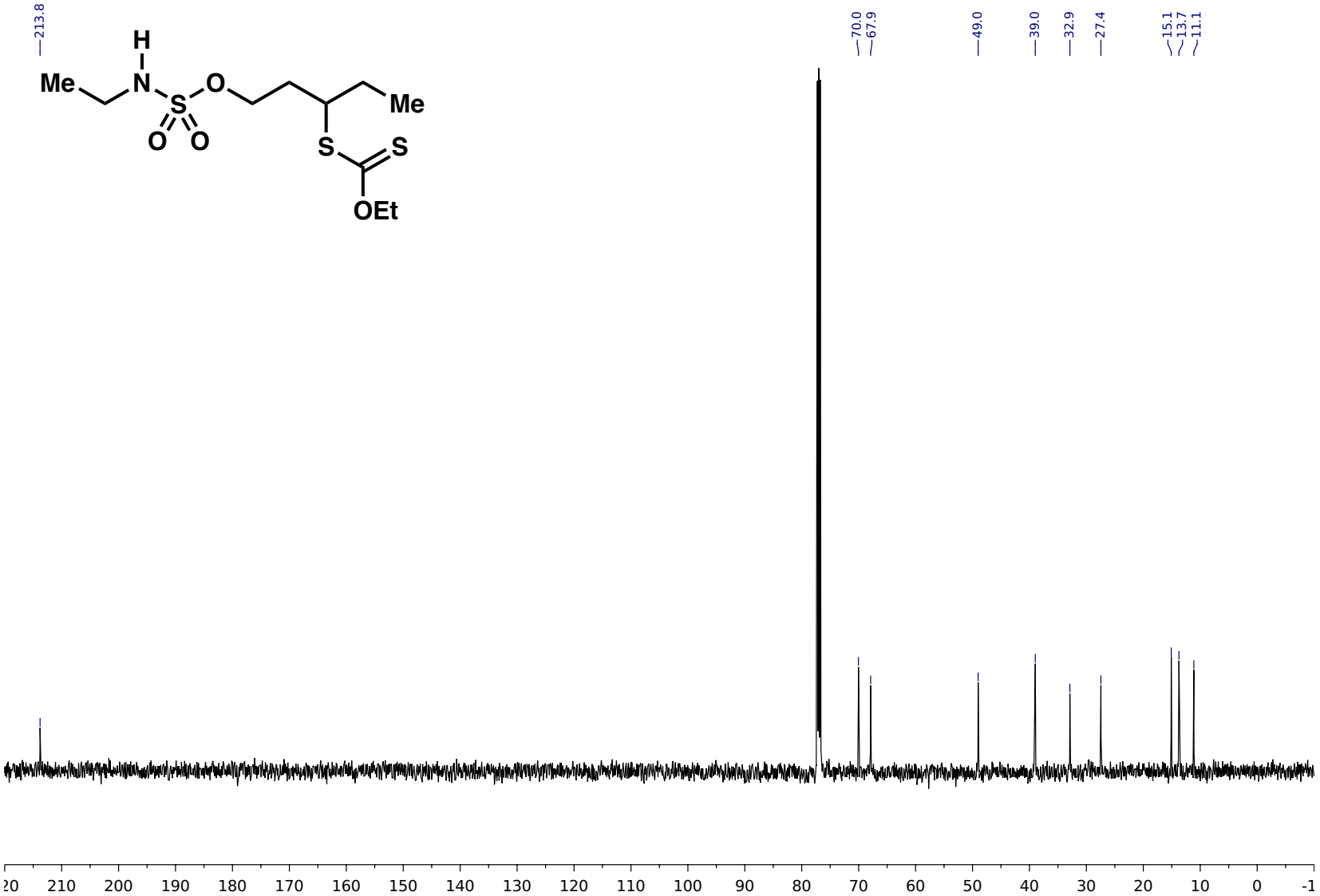
^{1}H NMR (400 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl *tert*-butylsulfamate (**2a**)



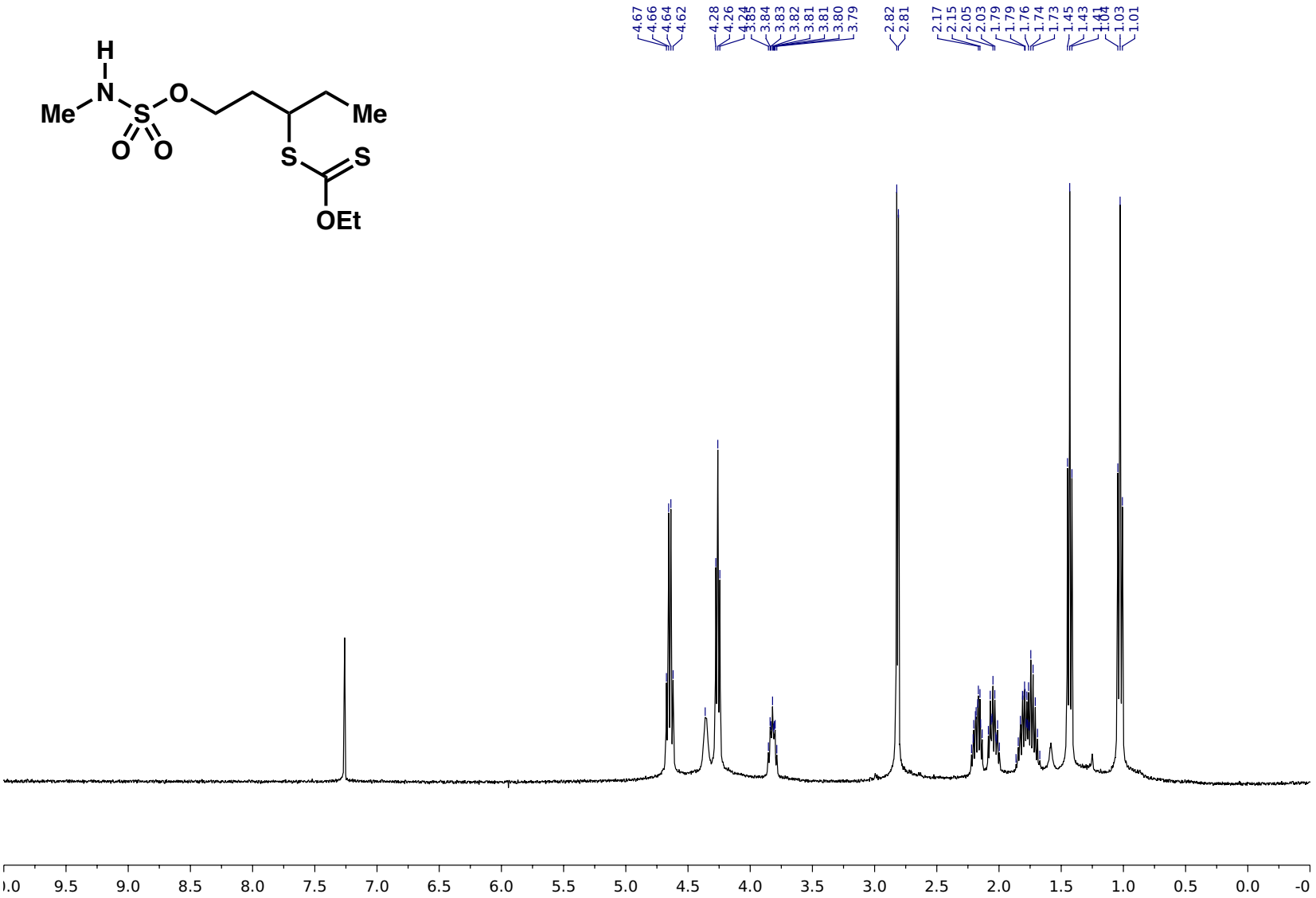
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl *tert*-butylsulfamate (**2a**)



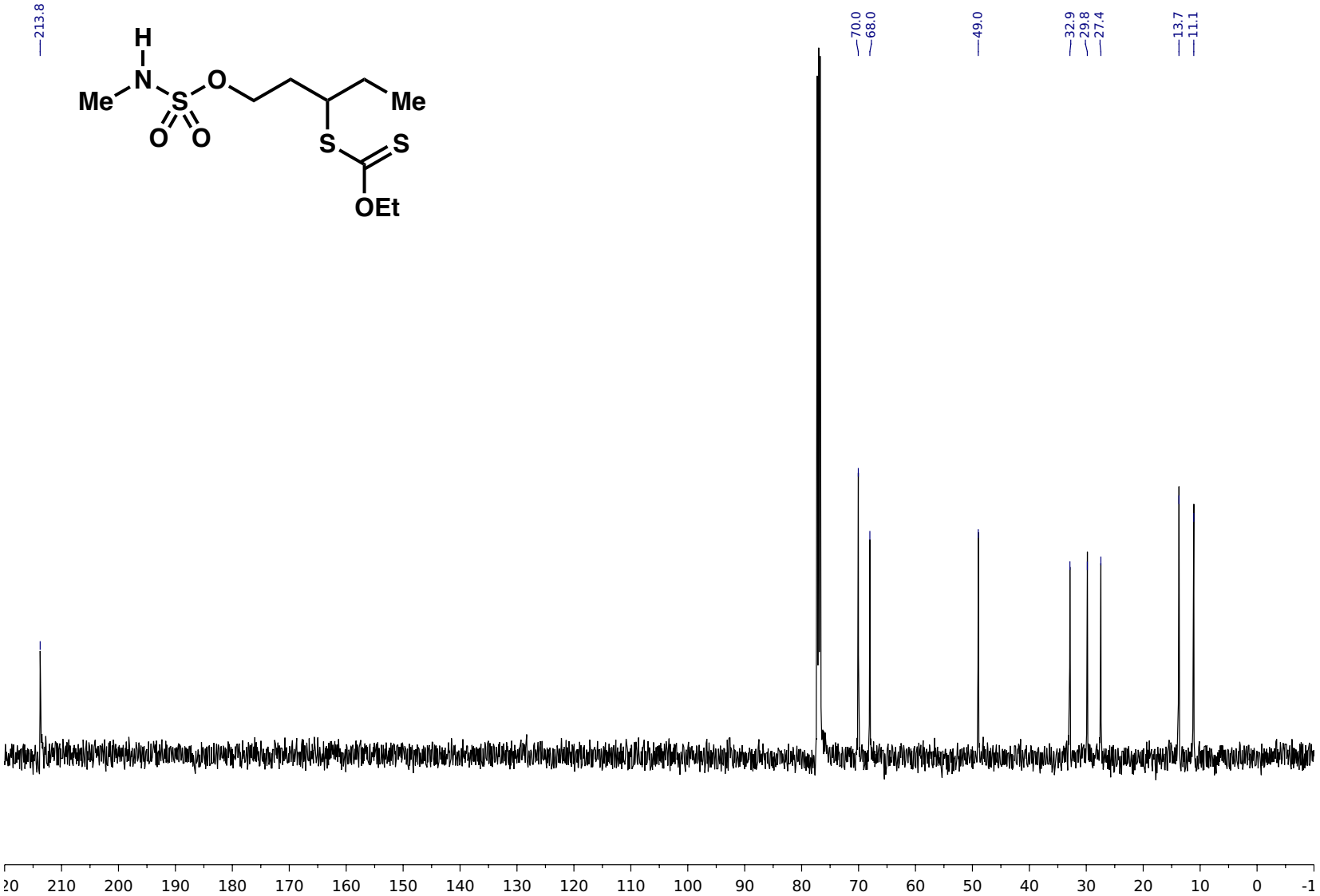
^{1}H NMR (400 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl ethylsulfamate (**2b**)



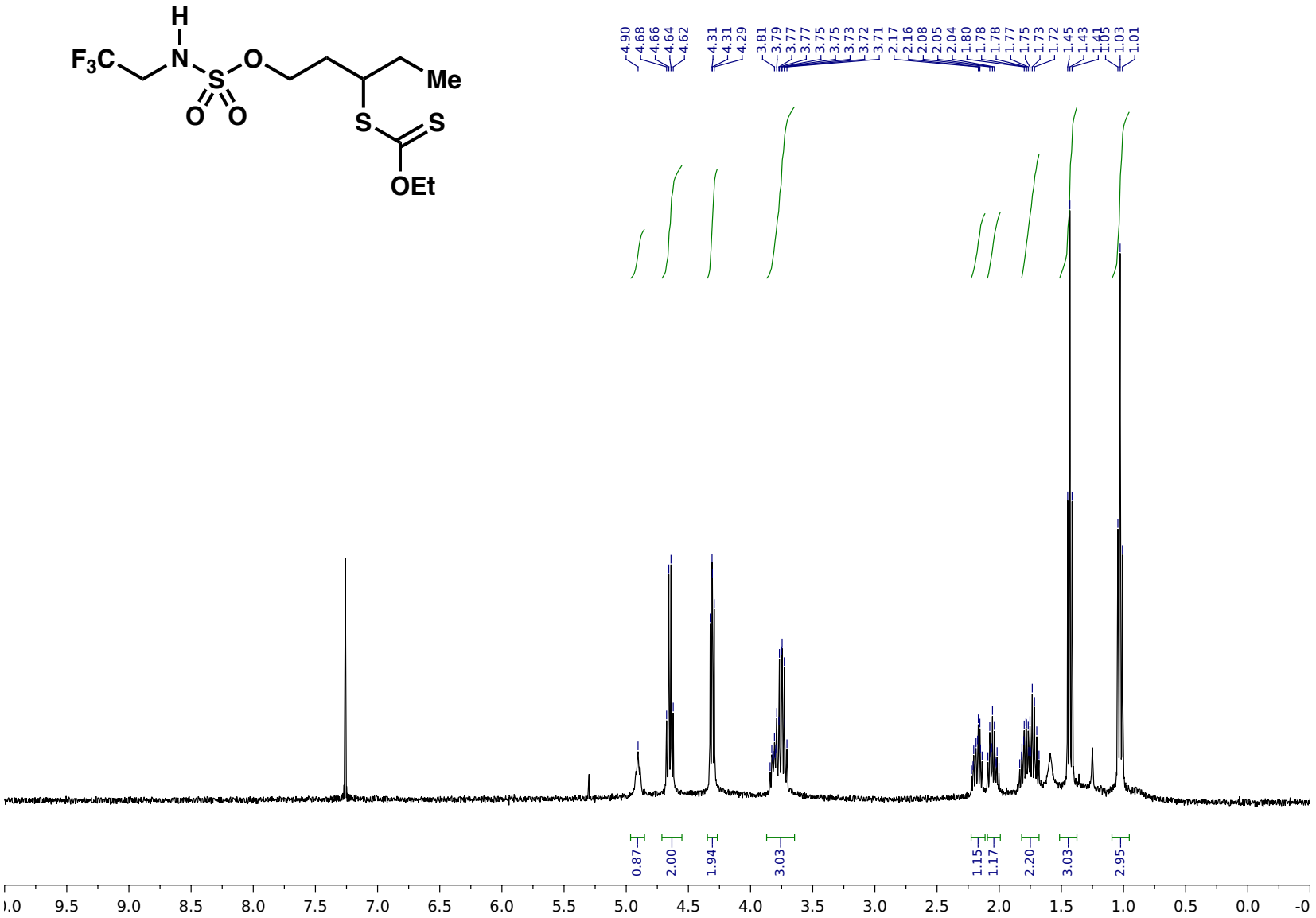
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl ethylsulfamate (**2b**)



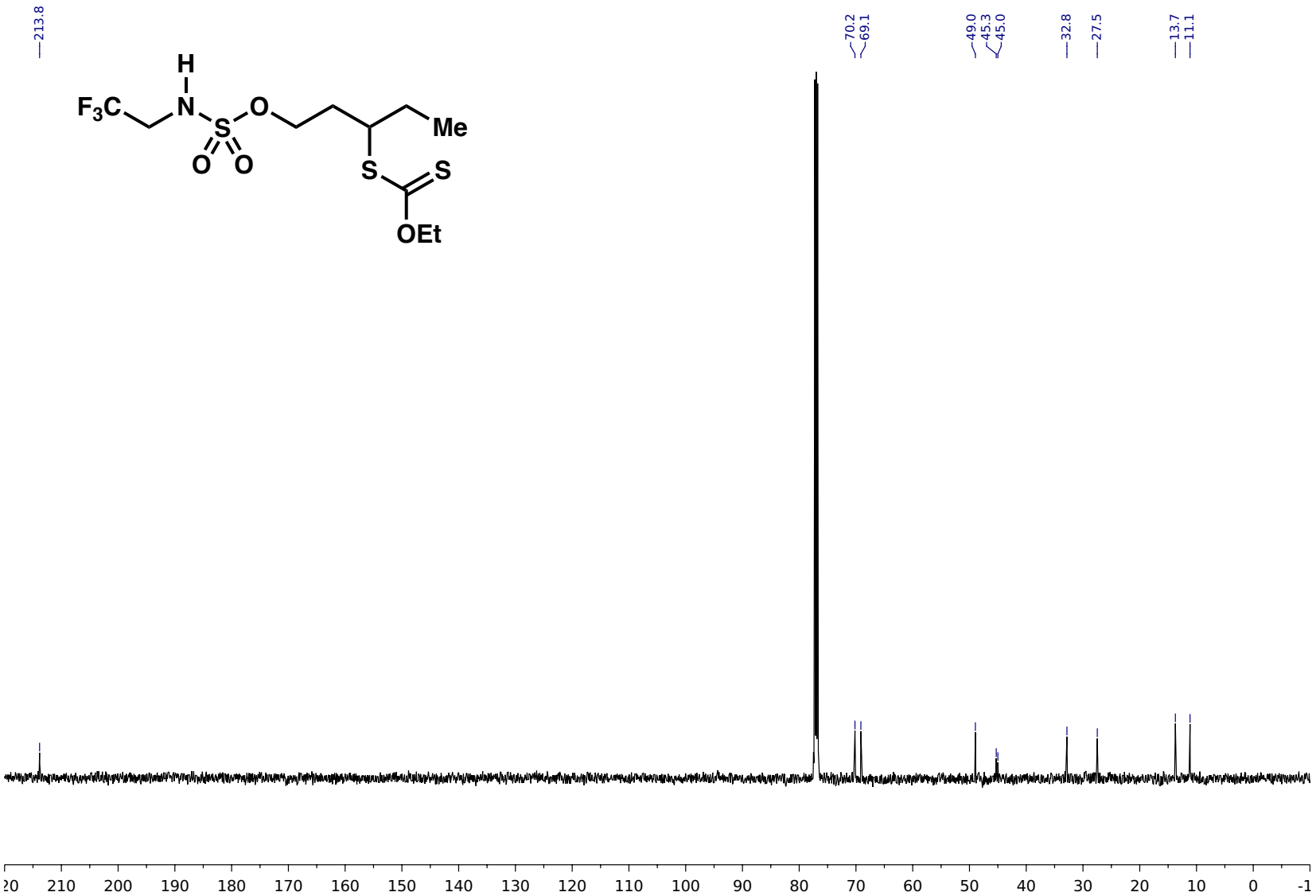
^{1}H NMR (400 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl methylsulfamate (**2c**)



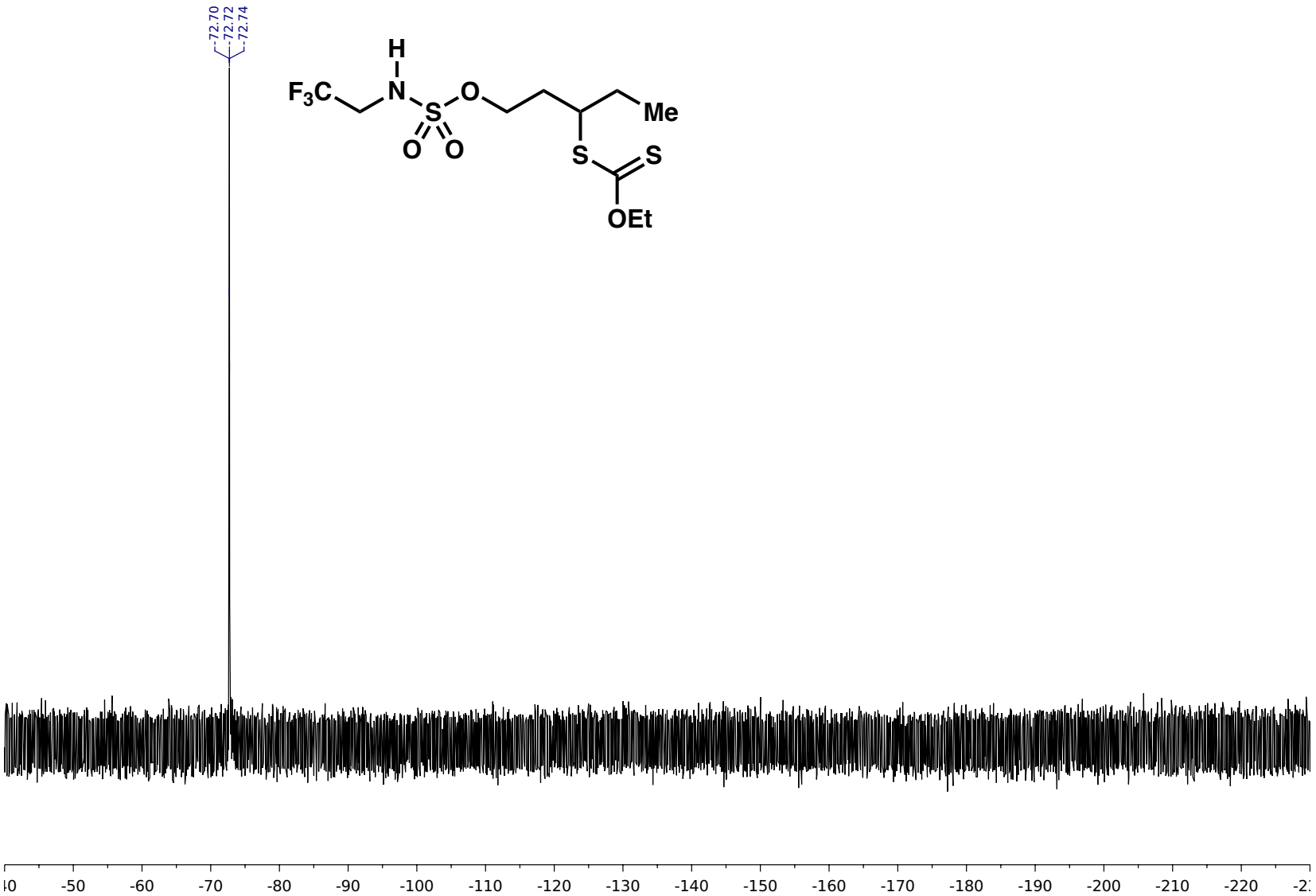
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl methylsulfamate (**2c**)



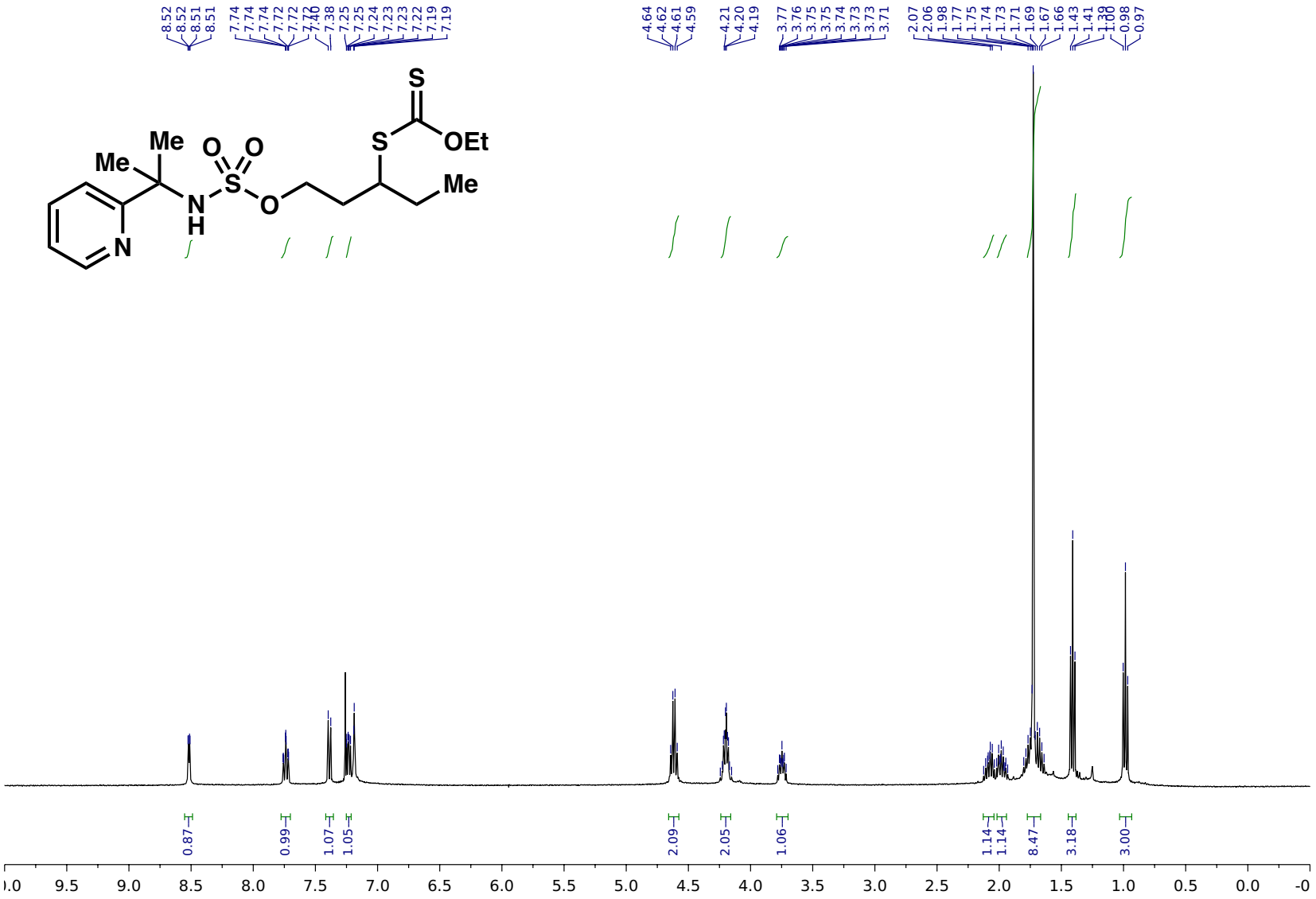
^{1}H NMR (400 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl (2,2,2-trichloroethyl)sulfamate (**2d**)



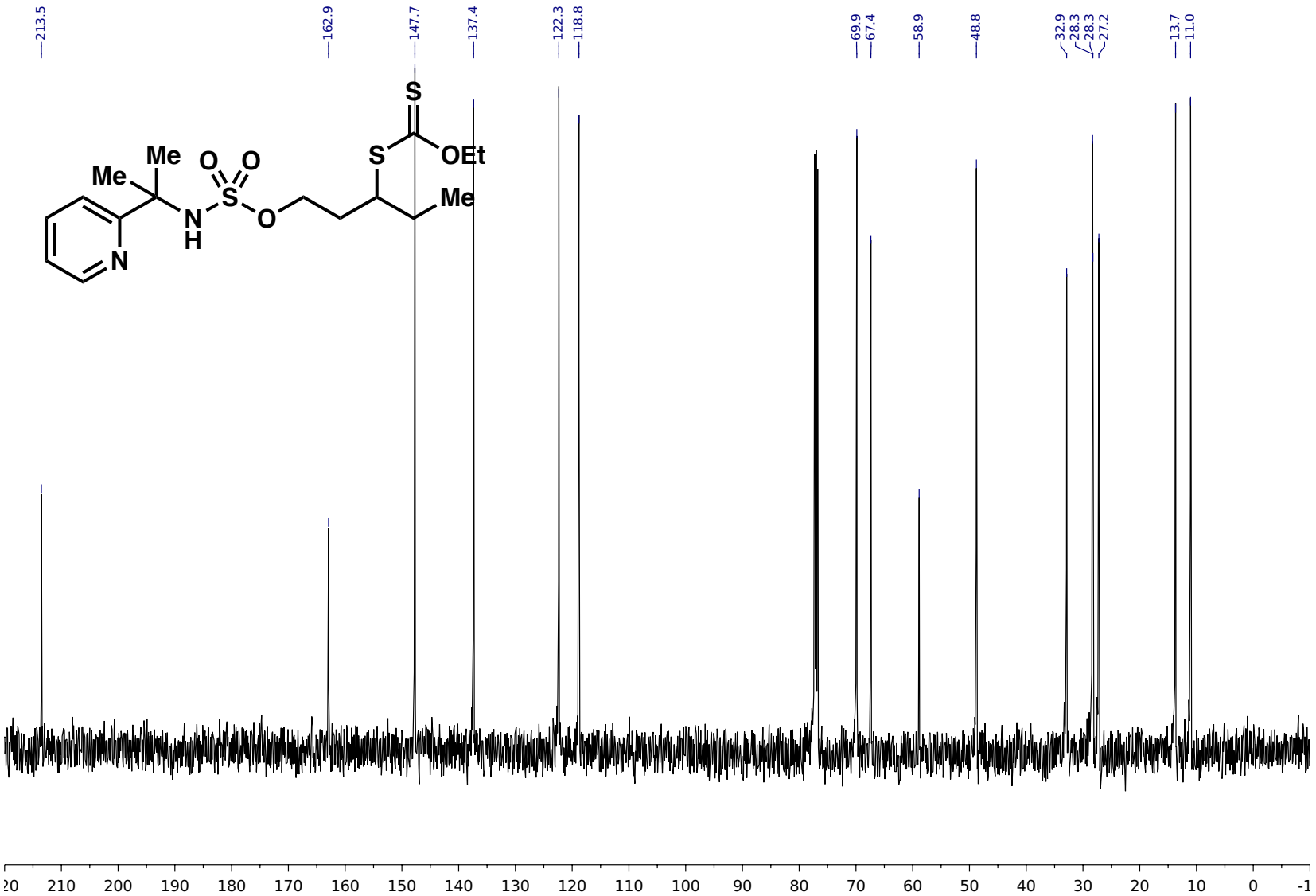
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl (2,2,2-trichloroethyl)sulfamate (**2d**)



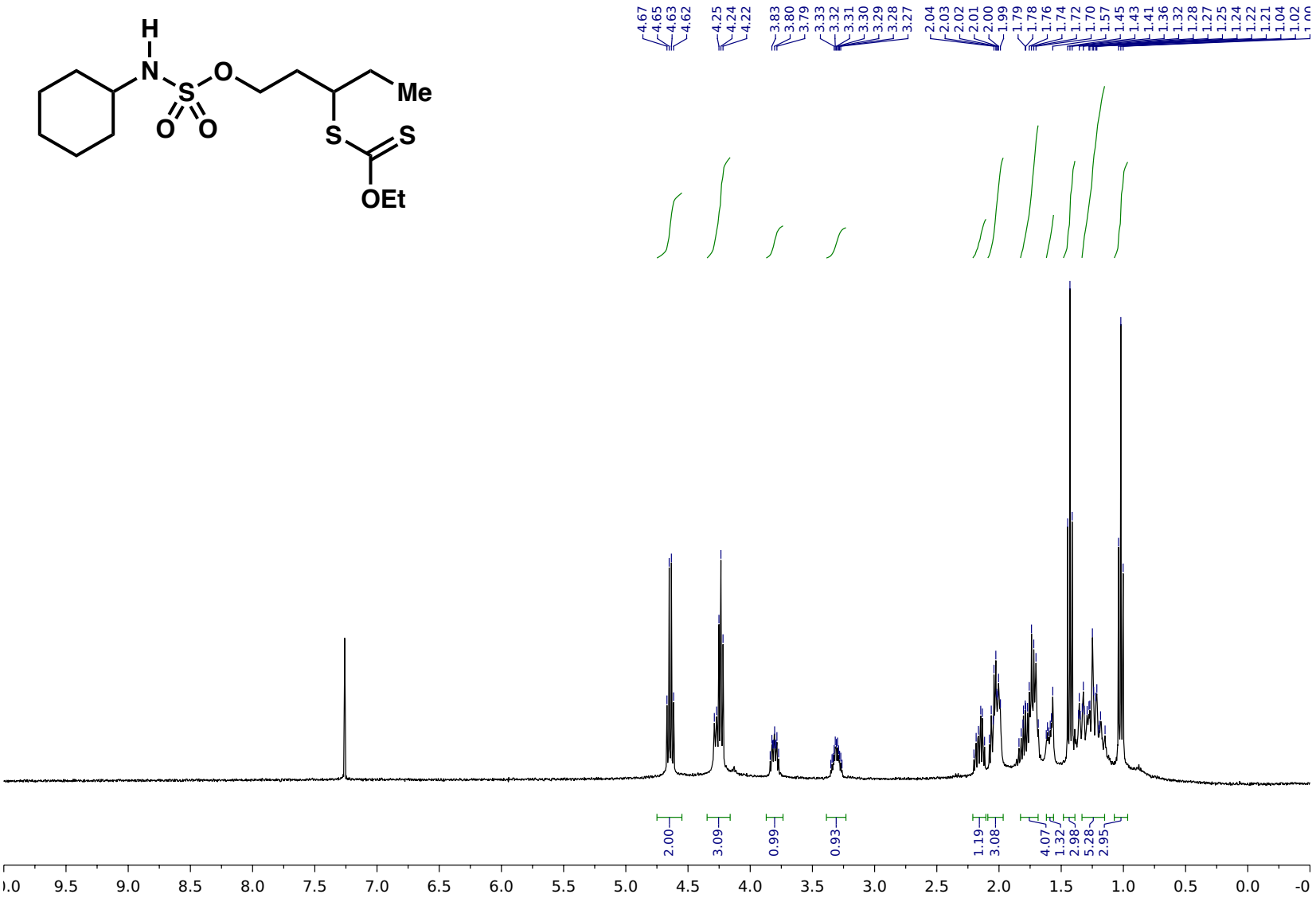
^{19}F NMR (376 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl (2,2,2-trichloroethyl)sulfamate (**2d**)



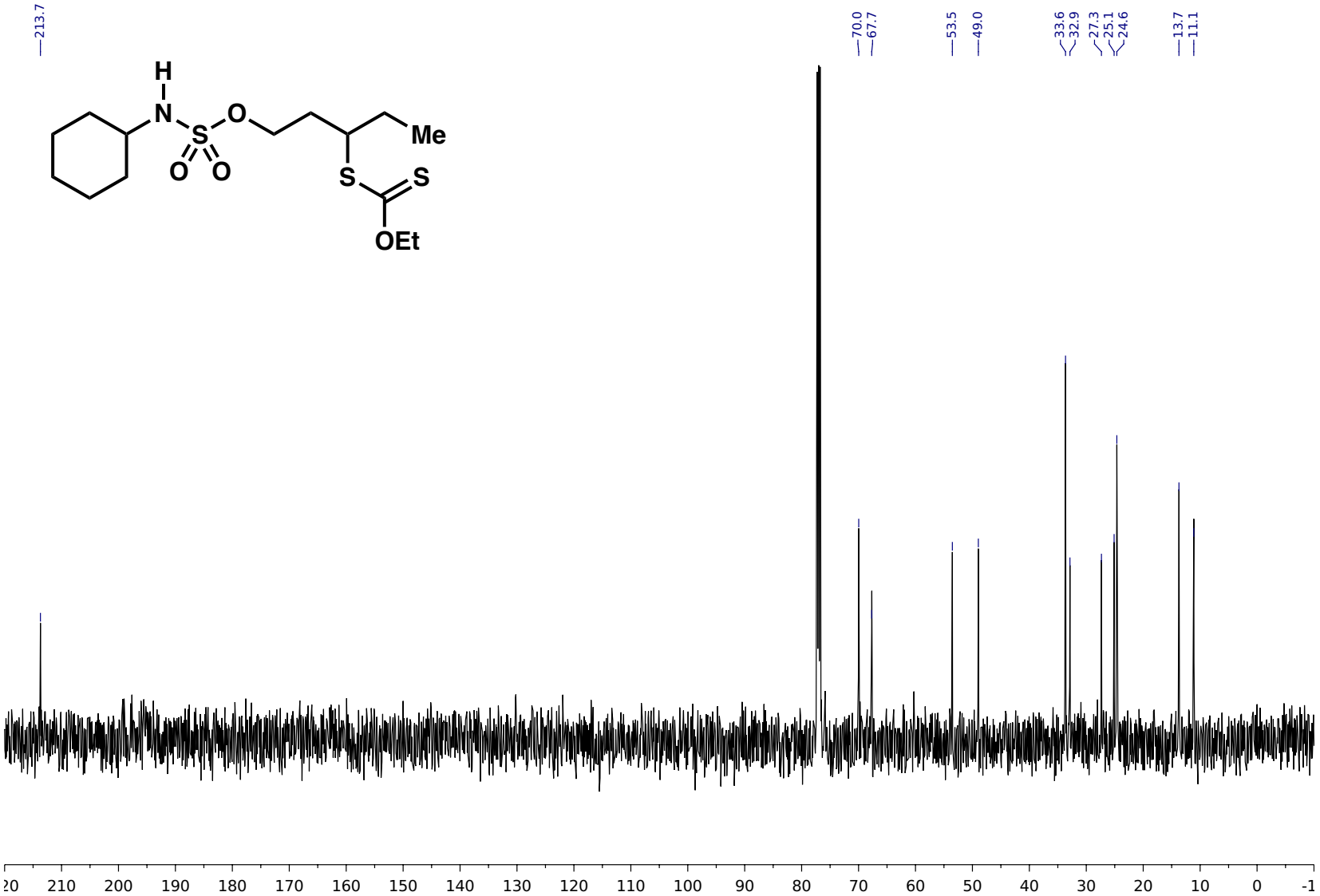
^{1}H NMR (400 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl 2-(pyridine-2-yl)propan-2-yl) sulfamate (**2e**)



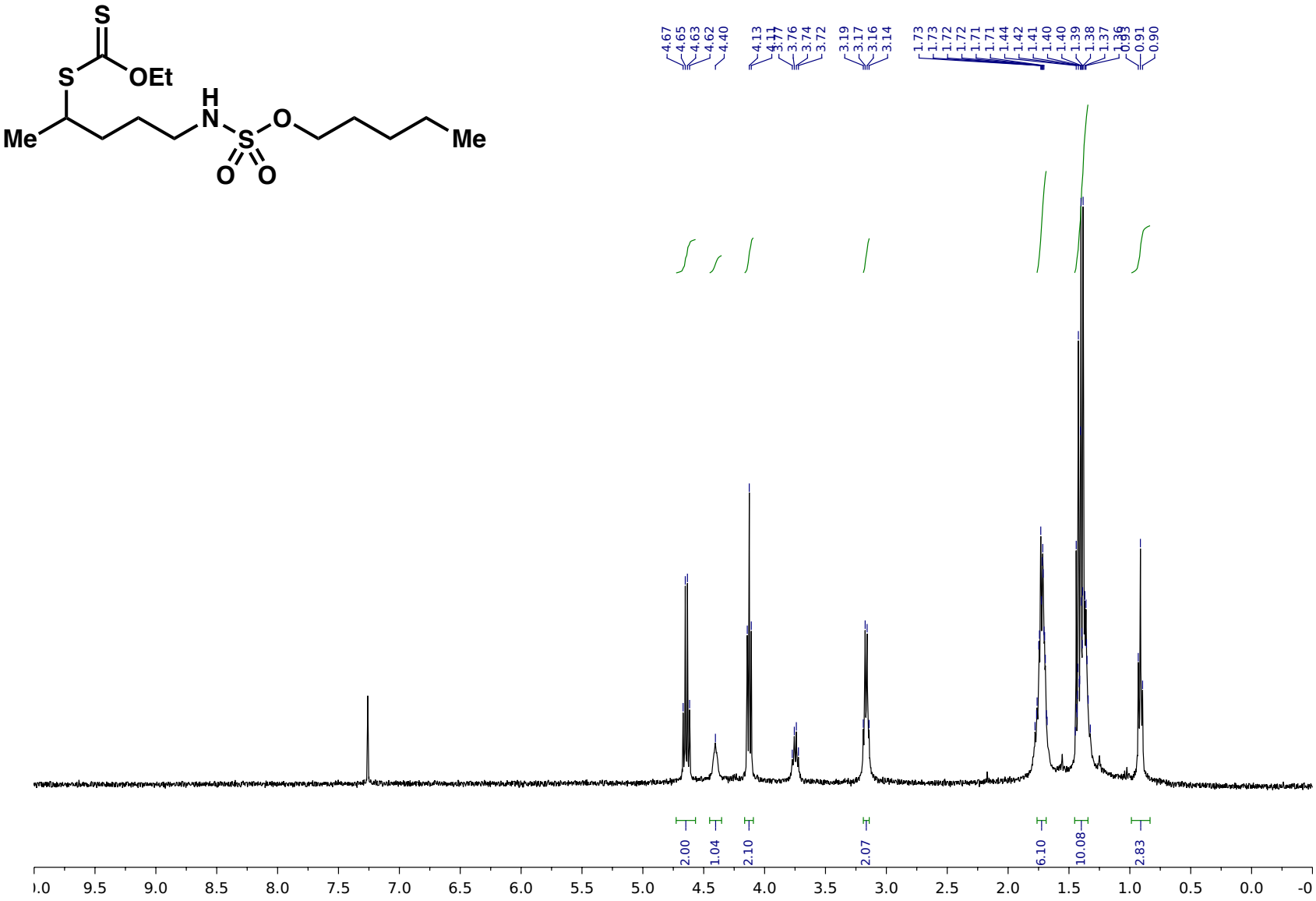
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl 2-(pyridine-2-yl)propan-2-yl) sulfamate (**2e**)



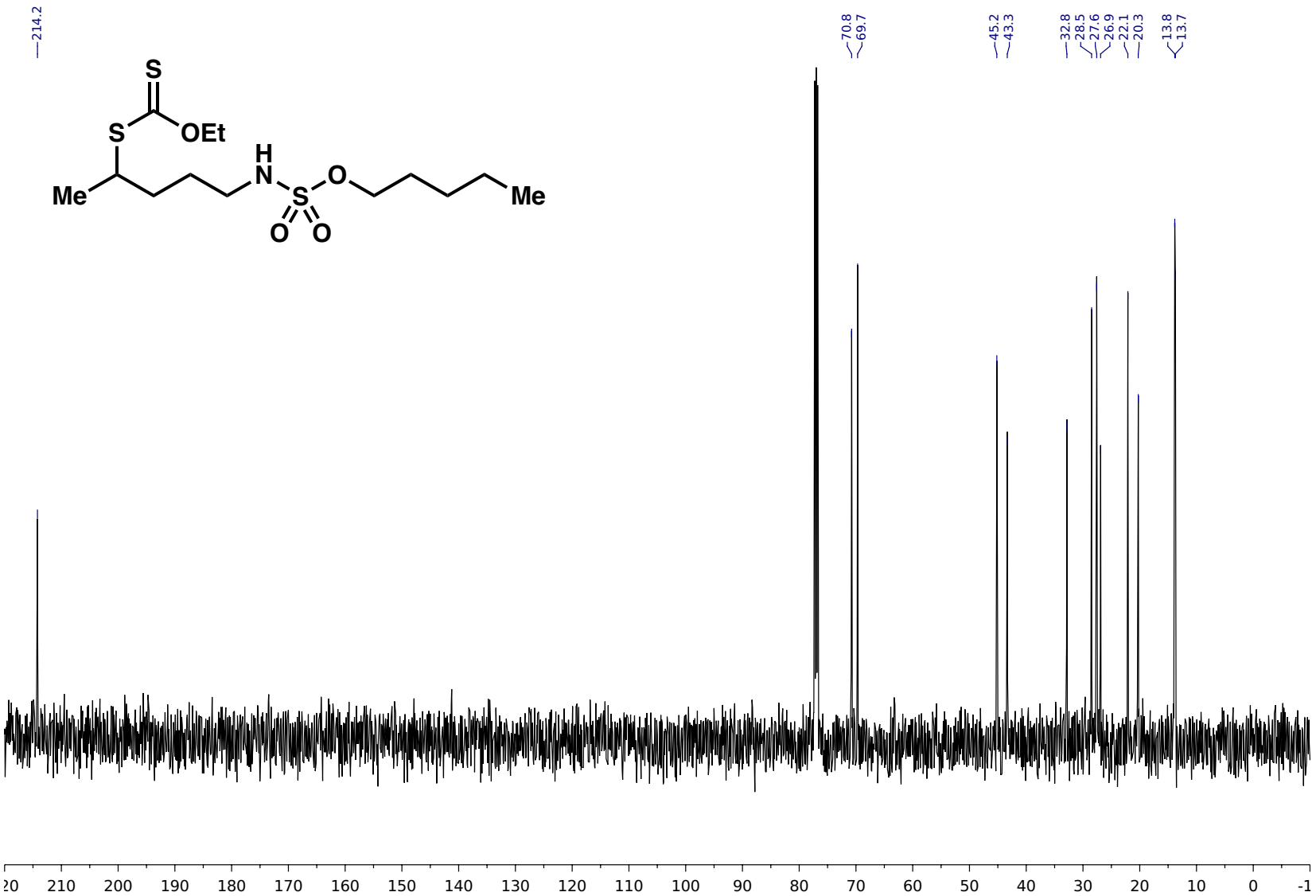
^{1}H NMR (400 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl cyclohexylsulfamate (**2f**)



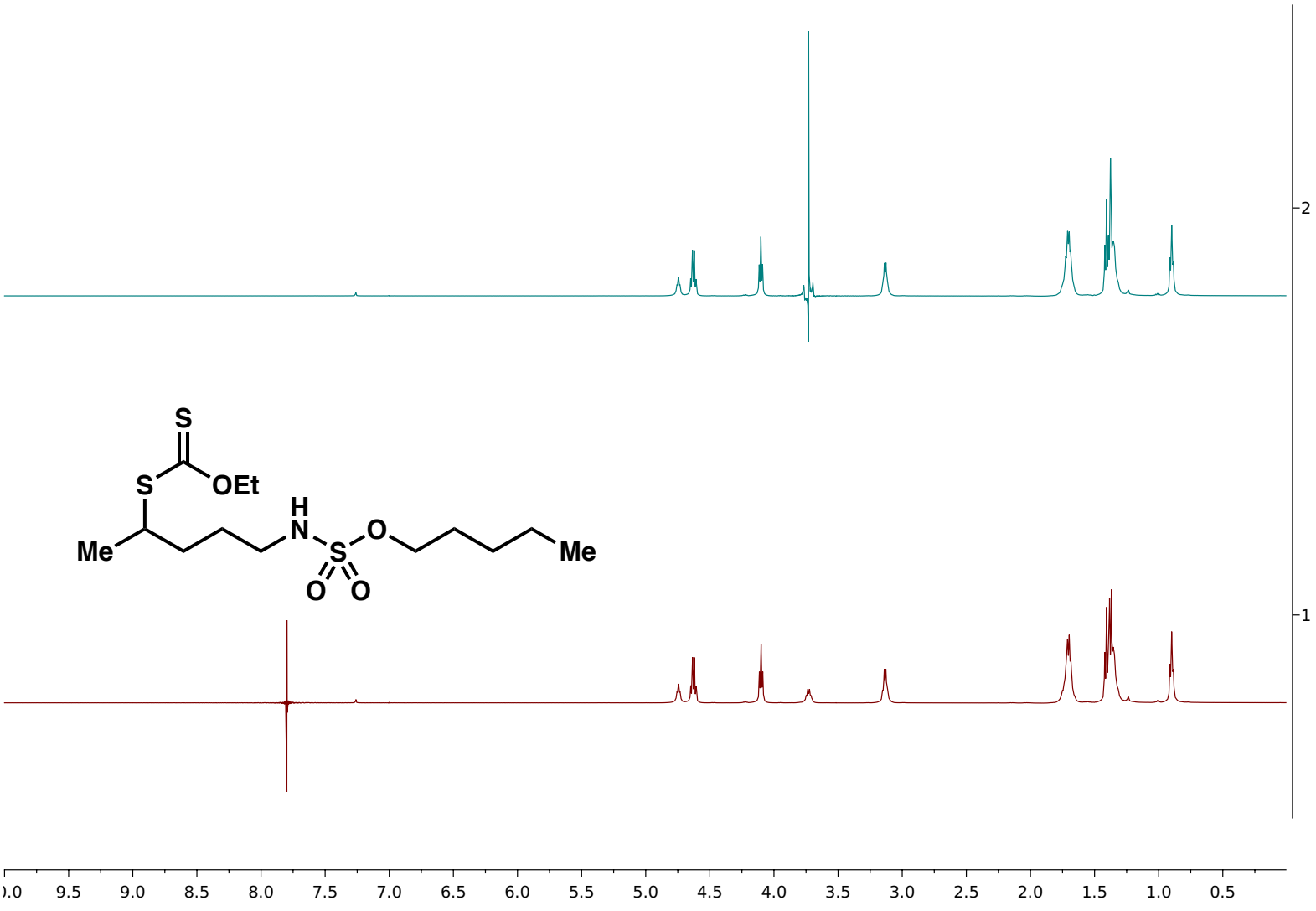
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl cyclohexylsulfamate (**2f**)



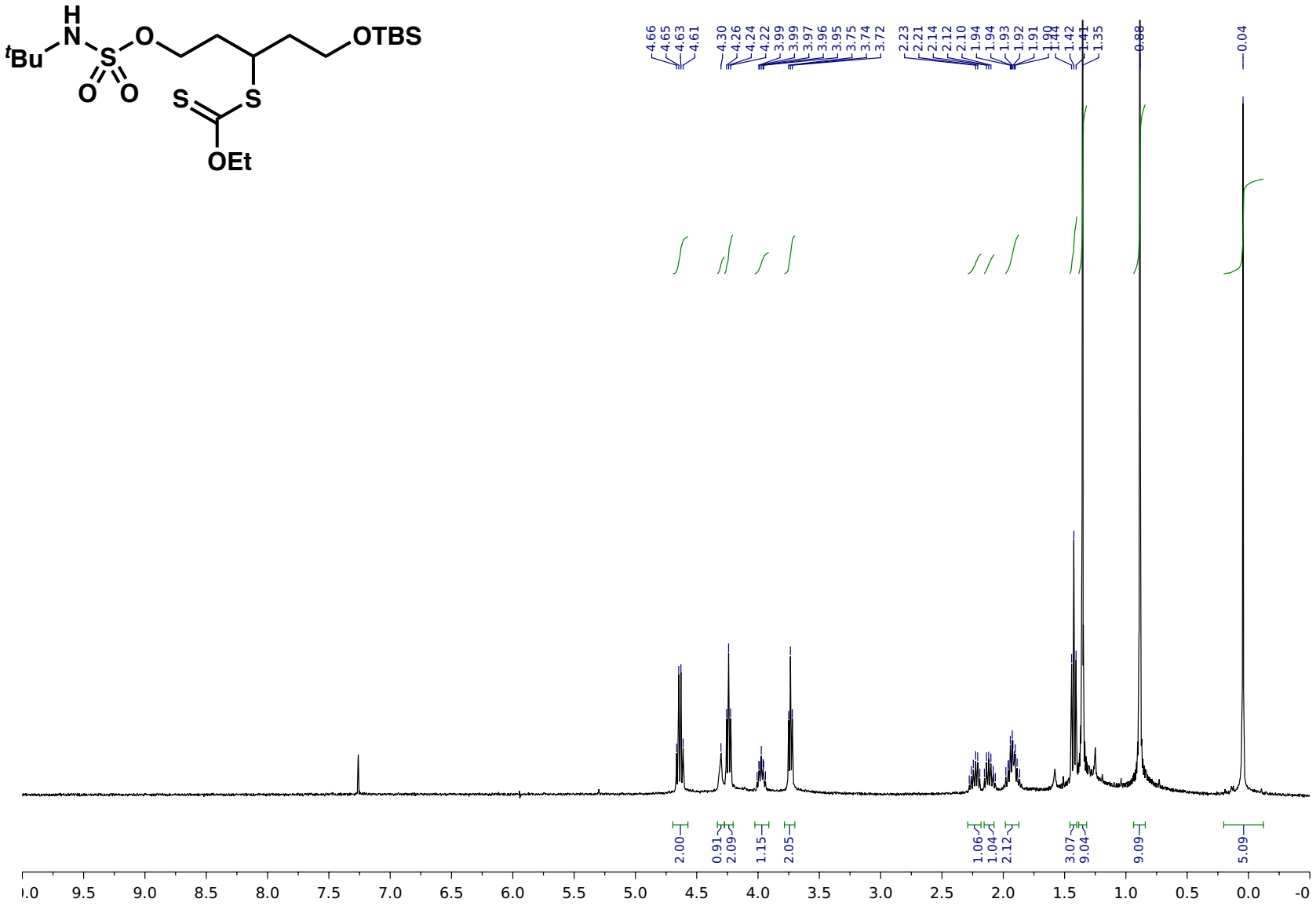
^{1}H NMR (400 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl pentylsulfamate (**4**)



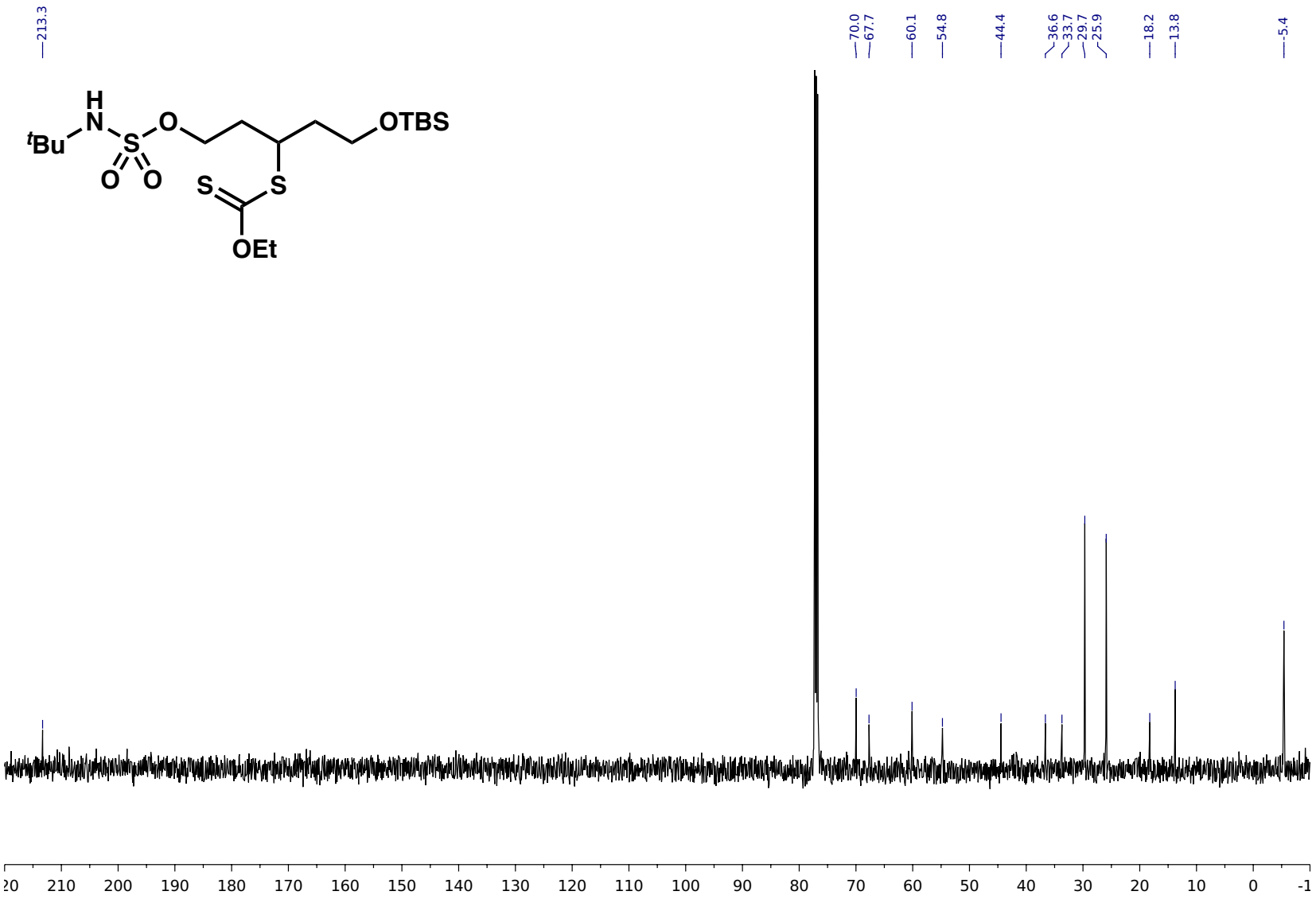
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl pentylsulfamate (**4**)



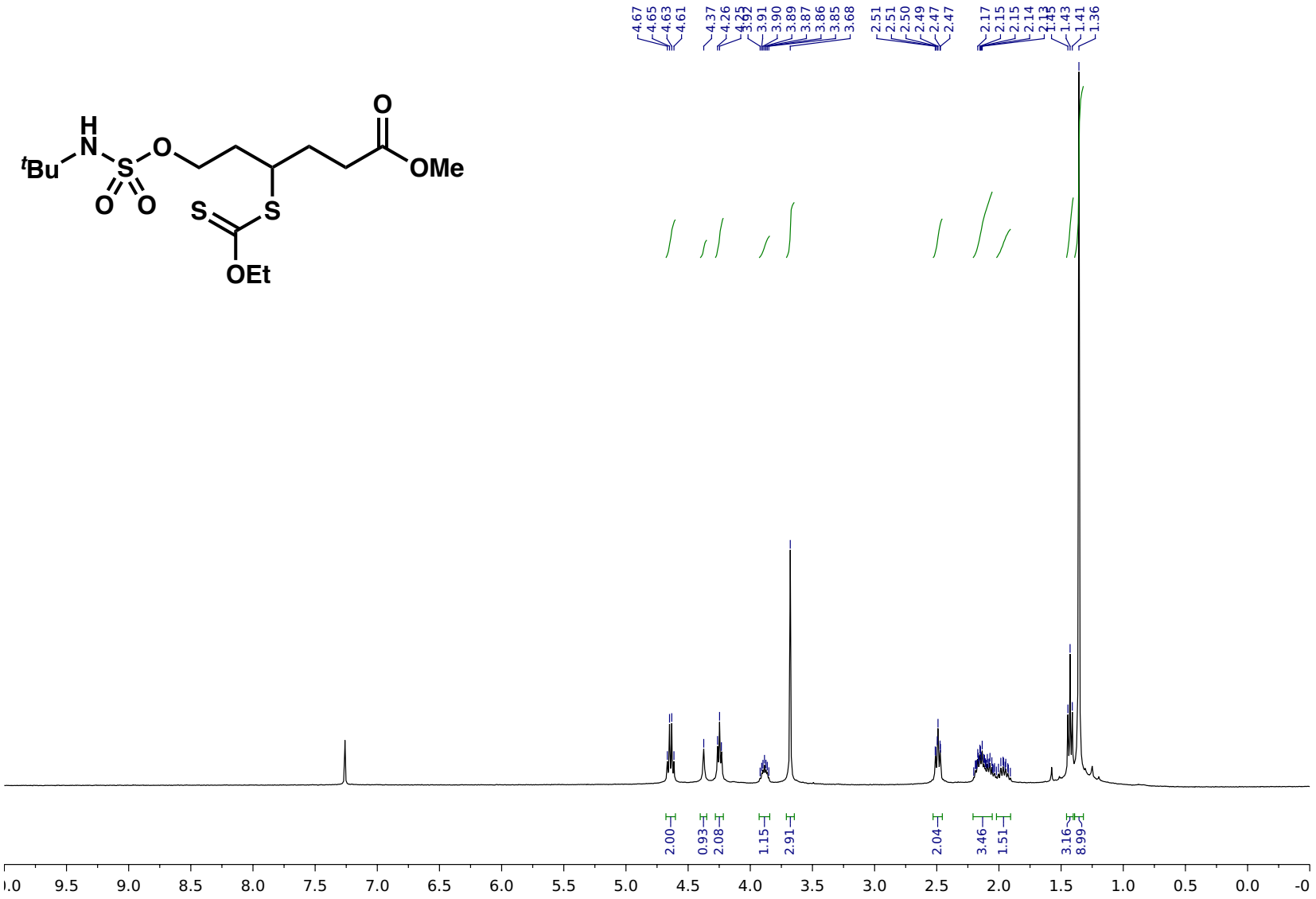
Homonuclear decoupling experiment for (**4**) [Bottom: Control Vs Top: Irradiation @ 3.73 ppm]



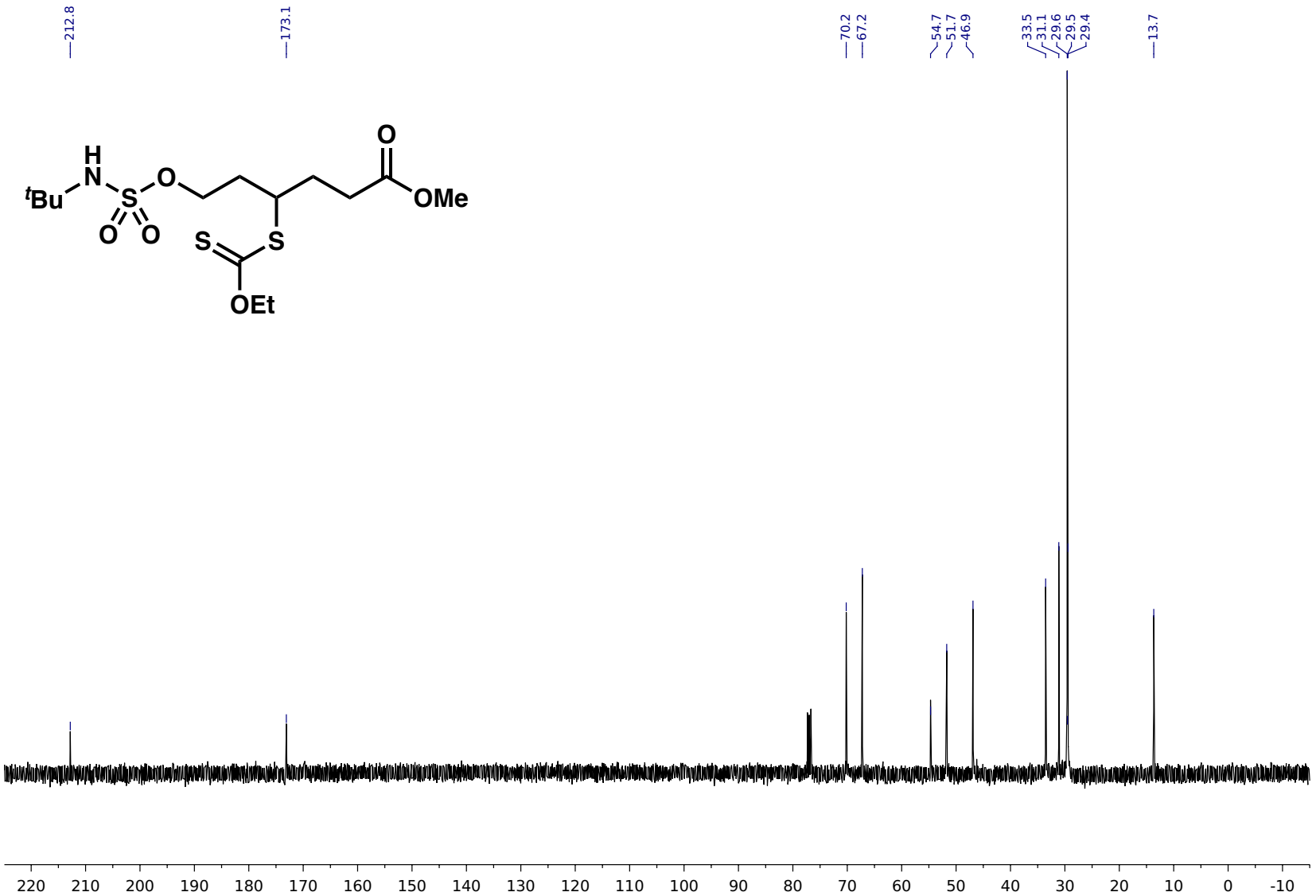
^{1}H NMR (400 MHz, $CDCl_3$) for 5-((*tert*-butyldimethylsilyl)oxy)-3-((ethoxycarbonothioyl)thio)pentyl *tert*-butylsulfamate **(2h)**



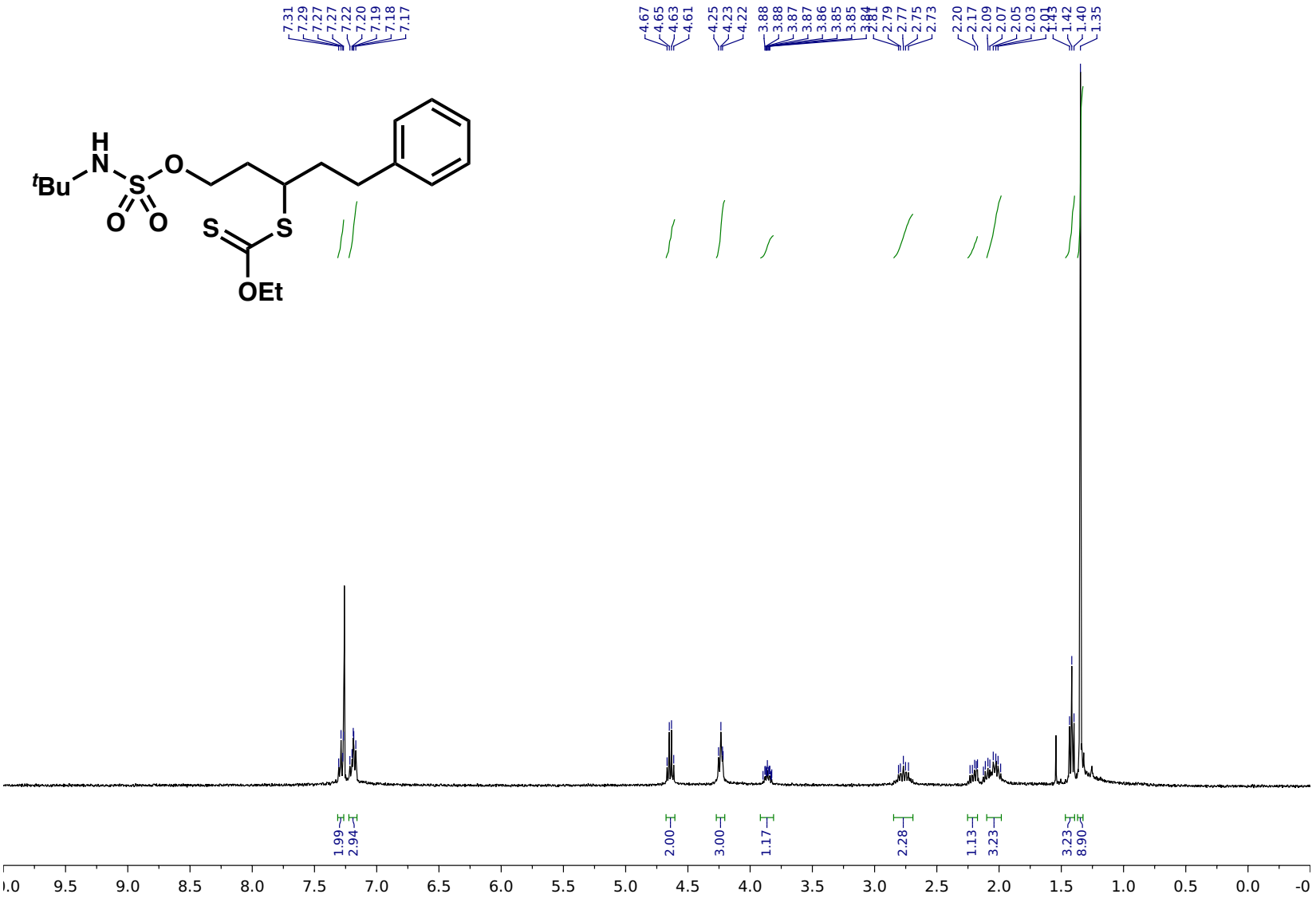
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 5-((*tert*-butyldimethylsilyl)oxy)-3-((ethoxycarbonothioyl)thio)pentyl *tert*-butylsulfamate **(2h)**



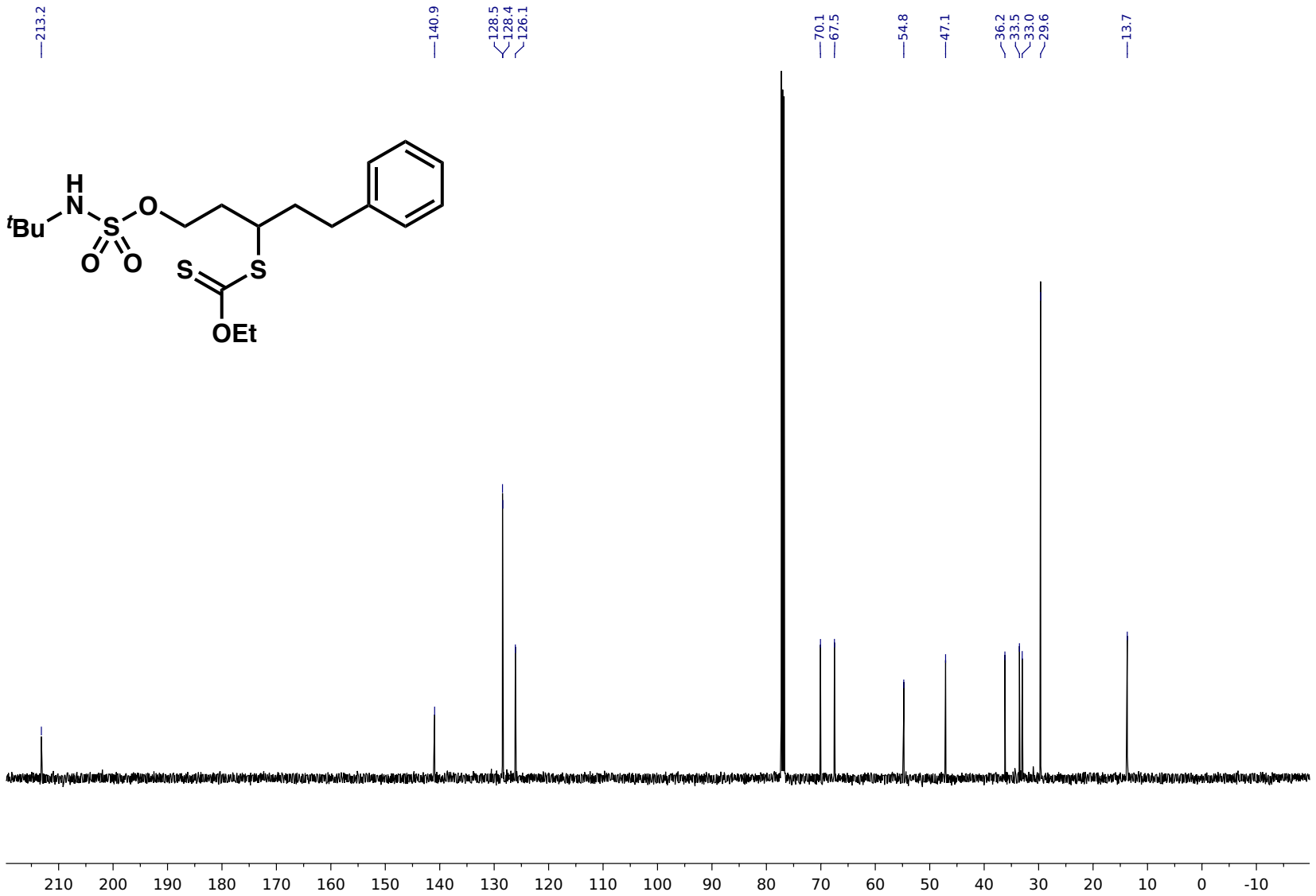
^{1}H NMR (400 MHz, $CDCl_3$) for methyl 4-((ethoxycarbonothioyl)thio)-6-hydroxyhexanoate) *tert*-butylsulfamate **(2i)**



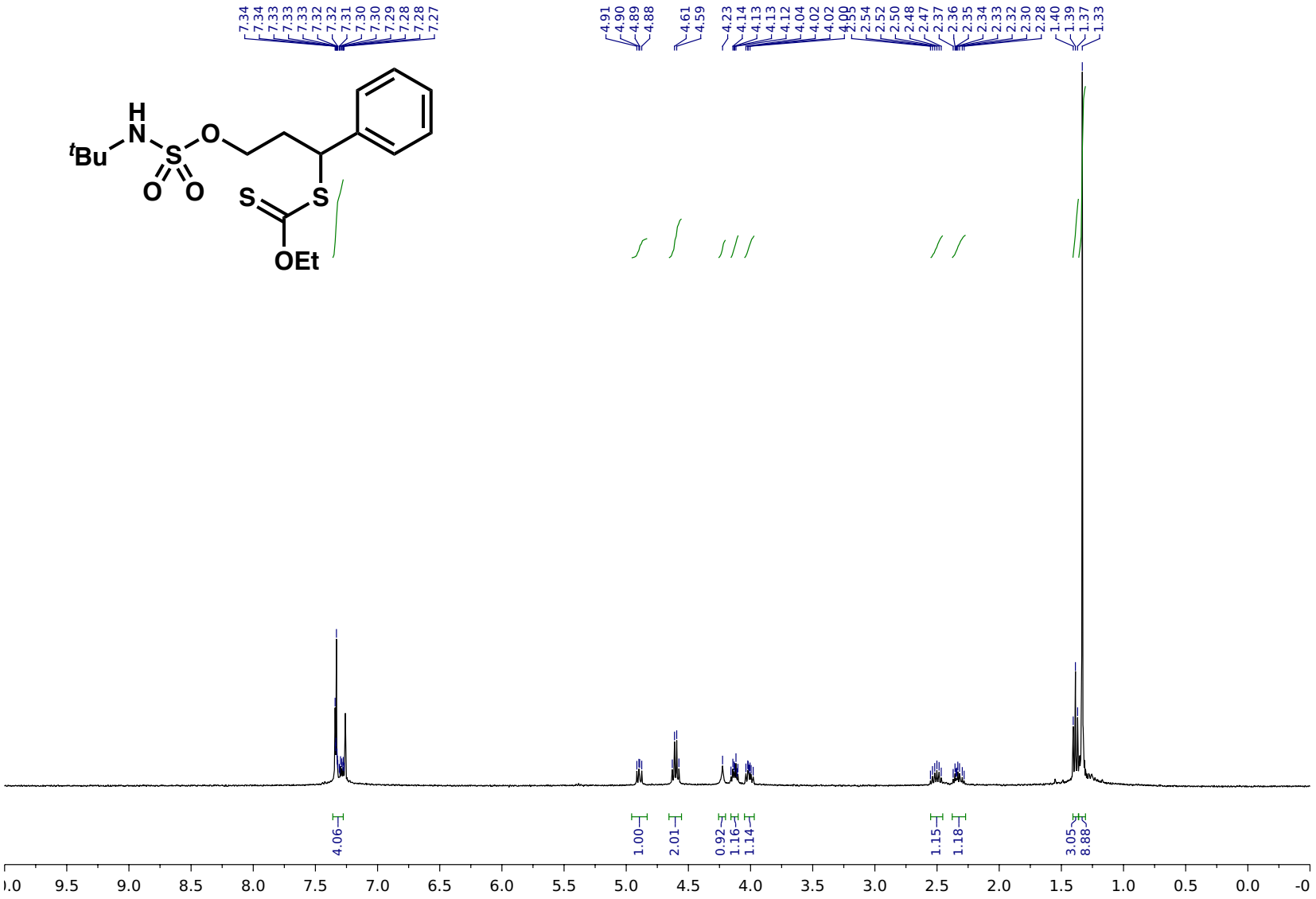
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for methyl 4-((ethoxycarbonothioyl)thio)-6-hydroxyhexanoate) *tert*-butylsulfamate **(2i)**



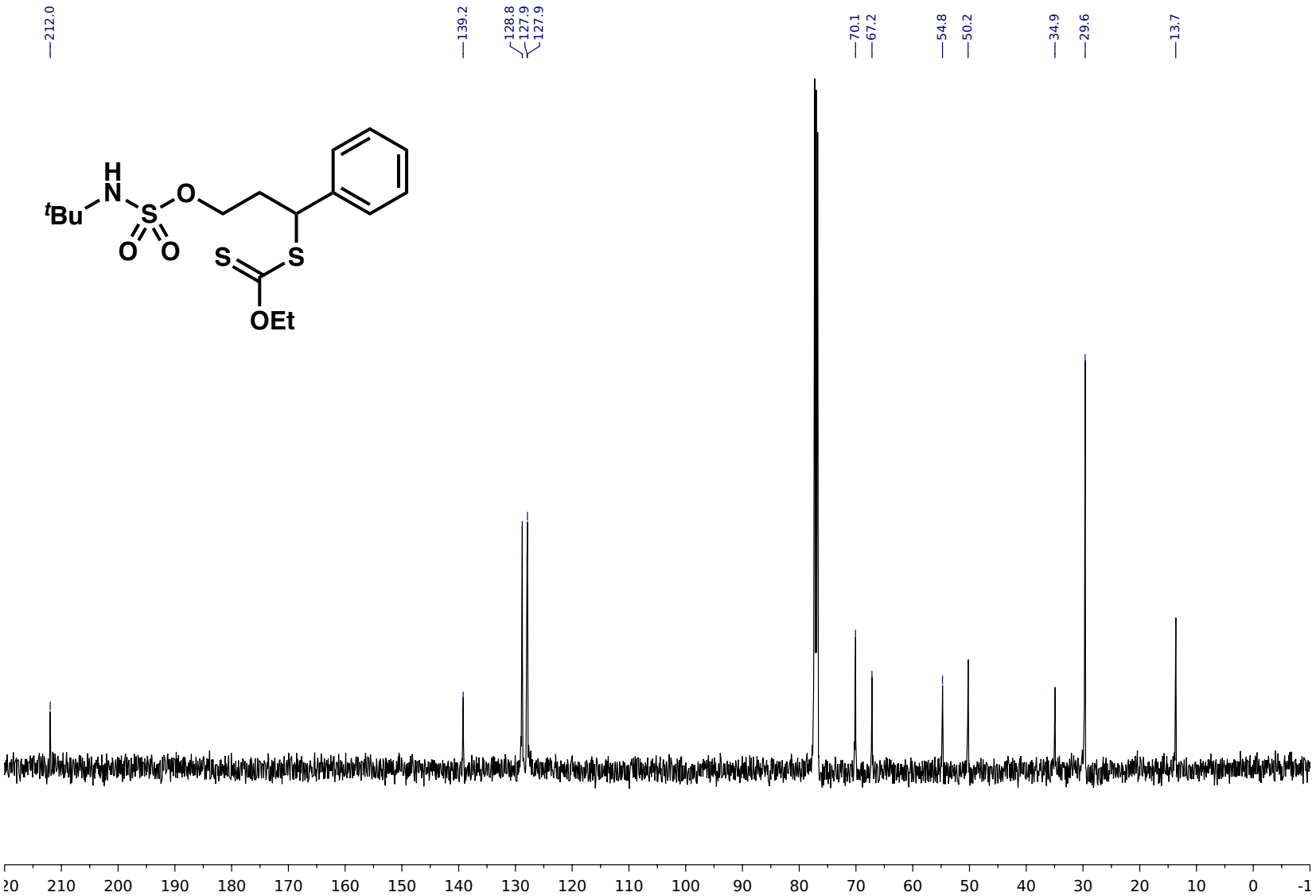
^{1}H NMR (400 MHz, $CDCl_3$) for 5-phenyl pentyl-3-((ethoxycarbonothioyl)thio)pentyl *tert*-butylsulfamate **(2j)**



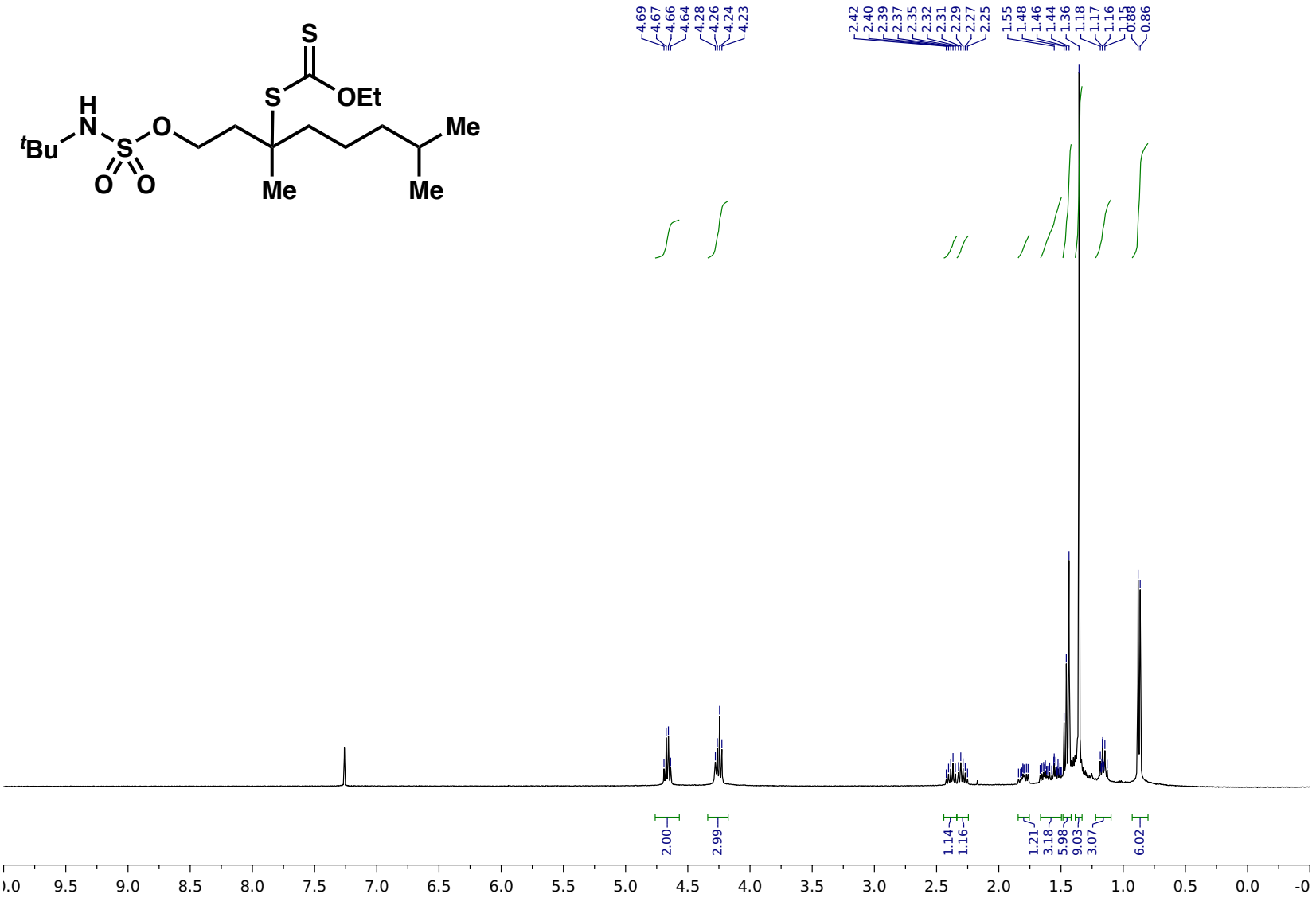
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 5-((*tert*-butyldimethylsilyl)oxy)-3-((ethoxycarbonothioyl)thio)pentyl *tert*-butylsulfamate **(2j)**



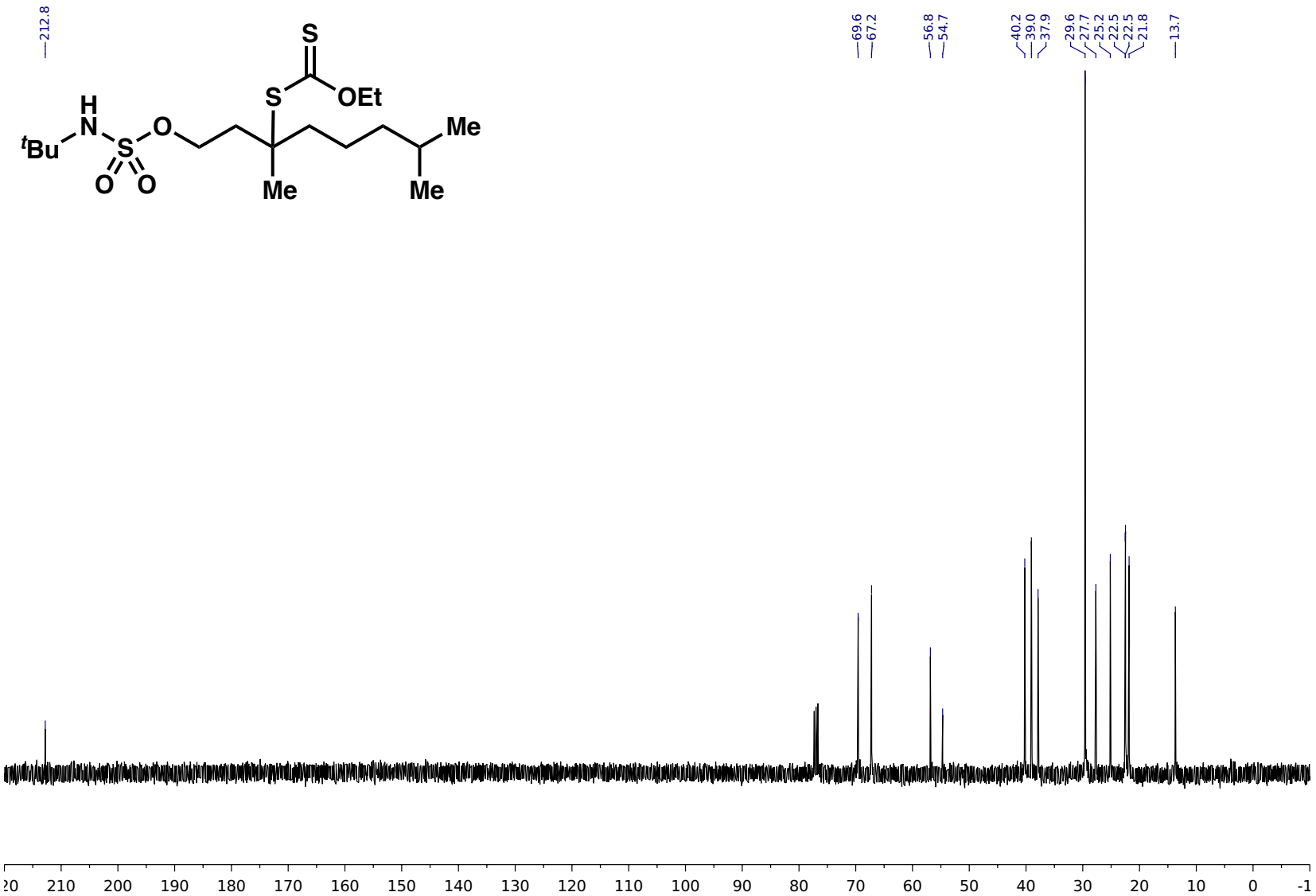
^{1}H NMR (400 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)-3-phenylpropyl *tert*-butylsulfamate **(2k)**



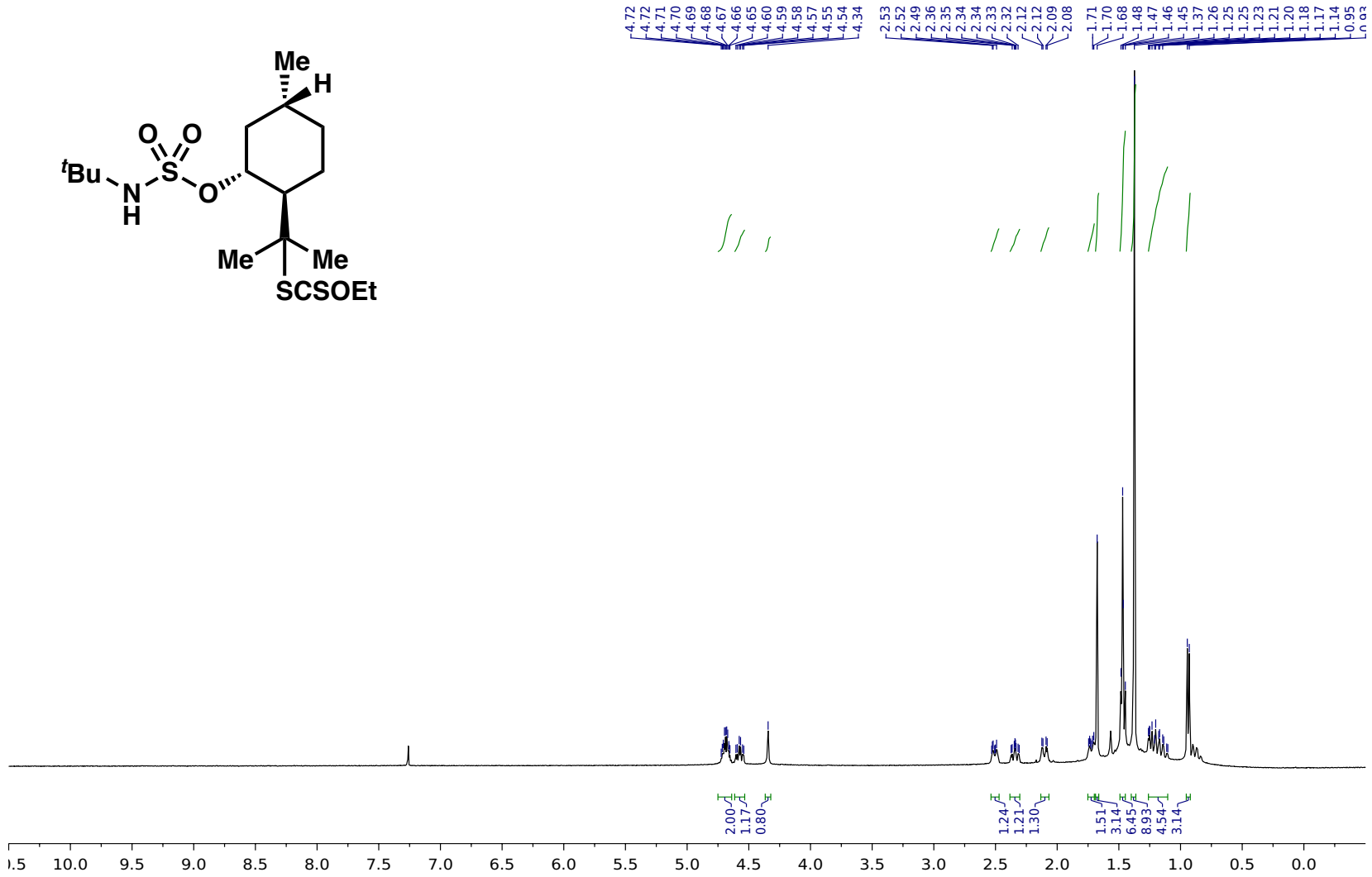
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)-3-phenylpropyl *tert*-butylsulfamate **(2k)**



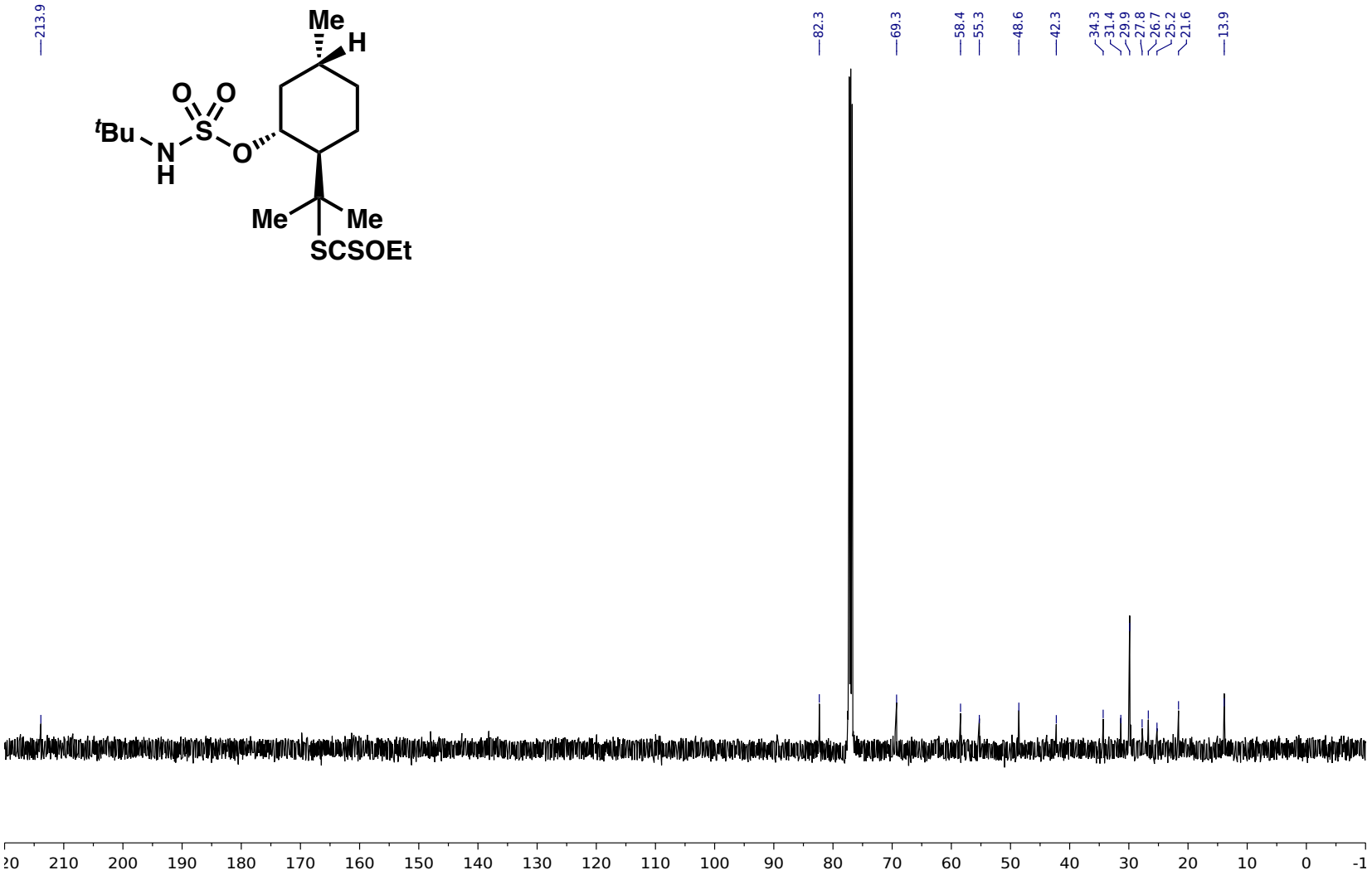
^{1}H NMR (400 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)-3,7-dimethyloctyl *tert*-butylsulfamate **(2l)**



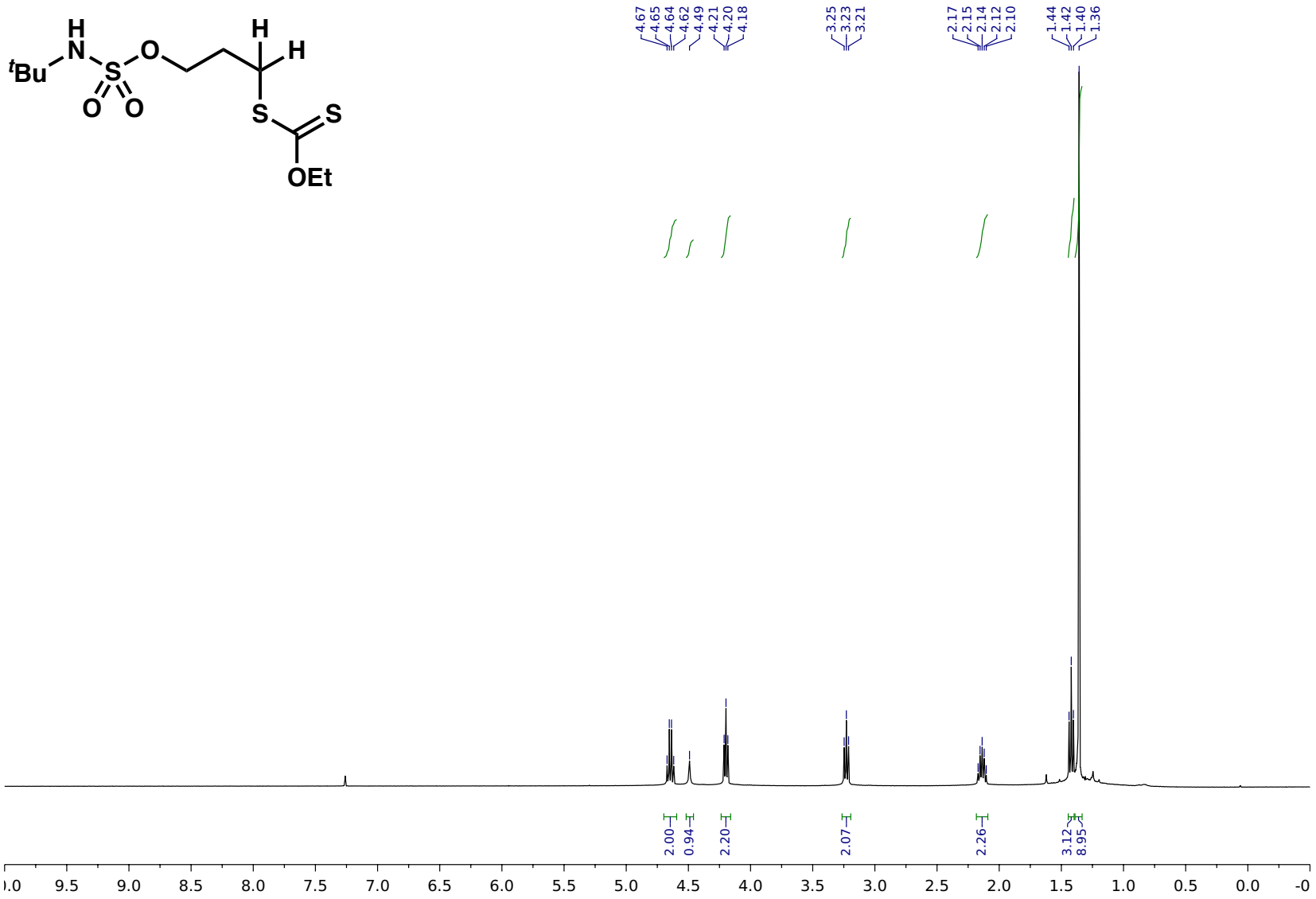
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)-3,7-dimethyloctyl *tert*-butylsulfamate **(2l)**



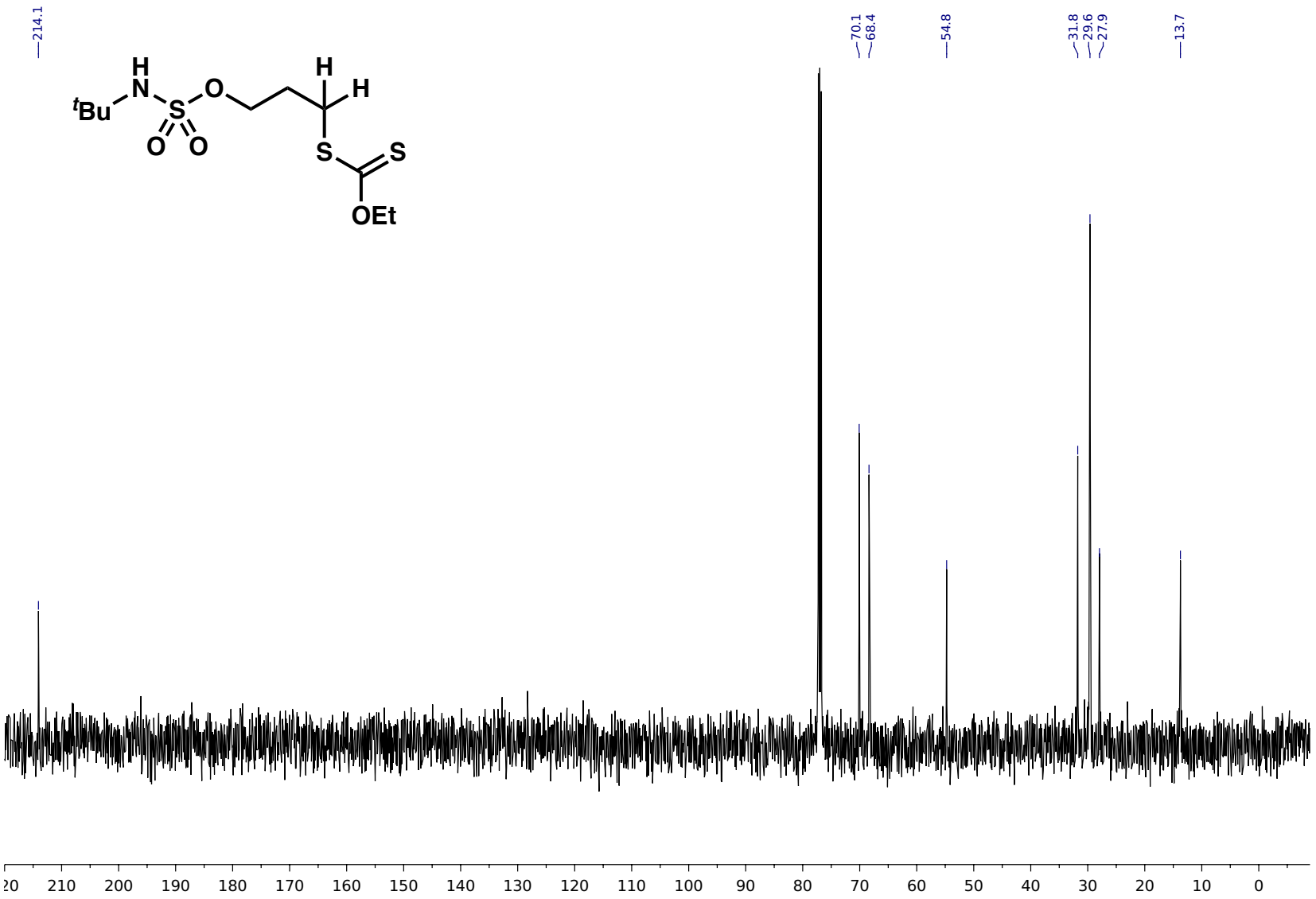
^{1}H NMR (400 MHz, $CDCl_3$) for (1*R*, 2*S*, 5*R*)-2-(2-(ethoxycarbonothioyl)thio)propan-2-yl)-5-methylcyclohexyl *tert*-butylsulfamate **(2m)**



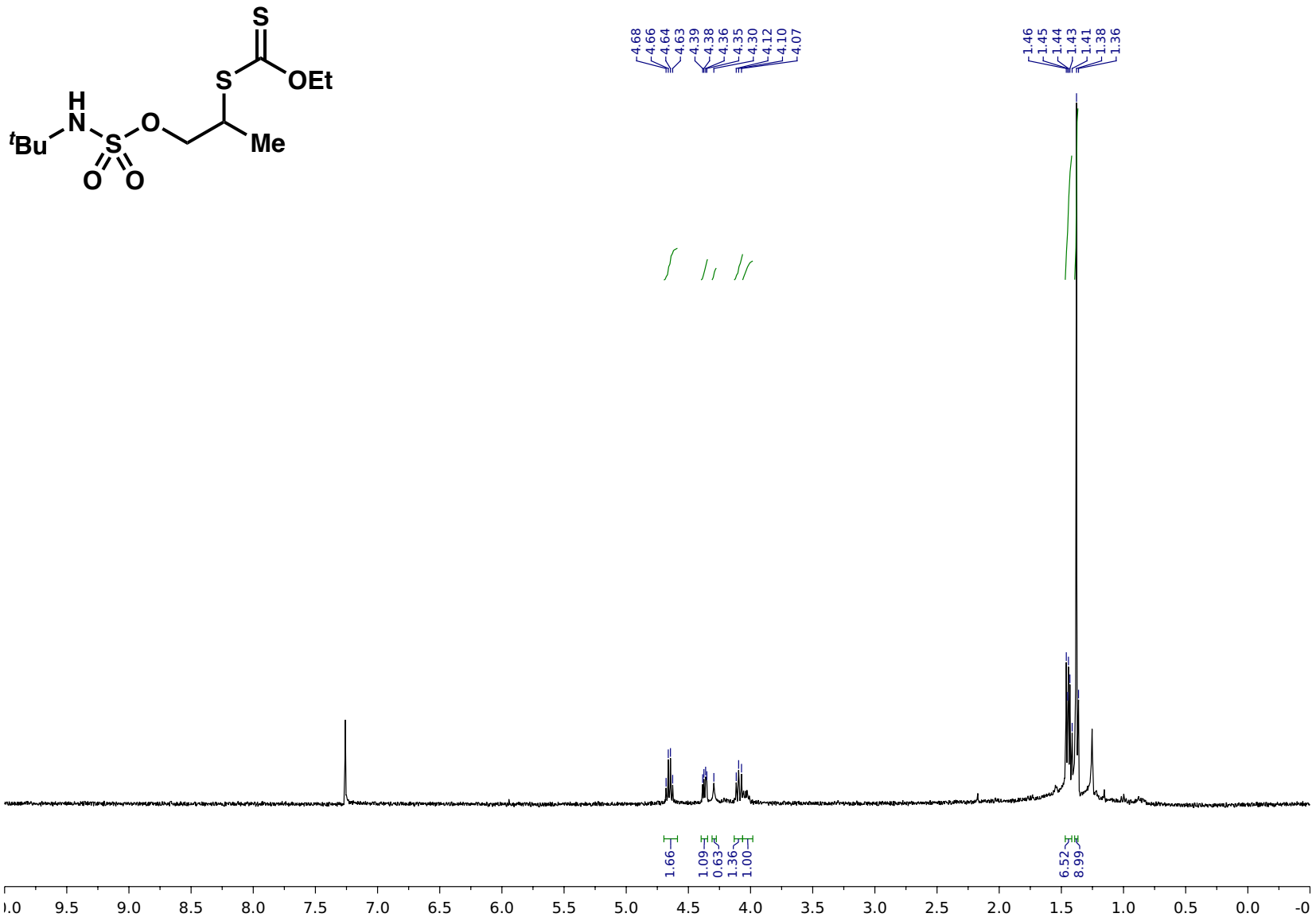
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for (1*R*, 2*R*, 5*R*)-2-(2-(ethoxycarbonothioyl)thio)propan-2-yl)-5-methylcyclohexyl *tert*-butylsulfamate **(2m)**



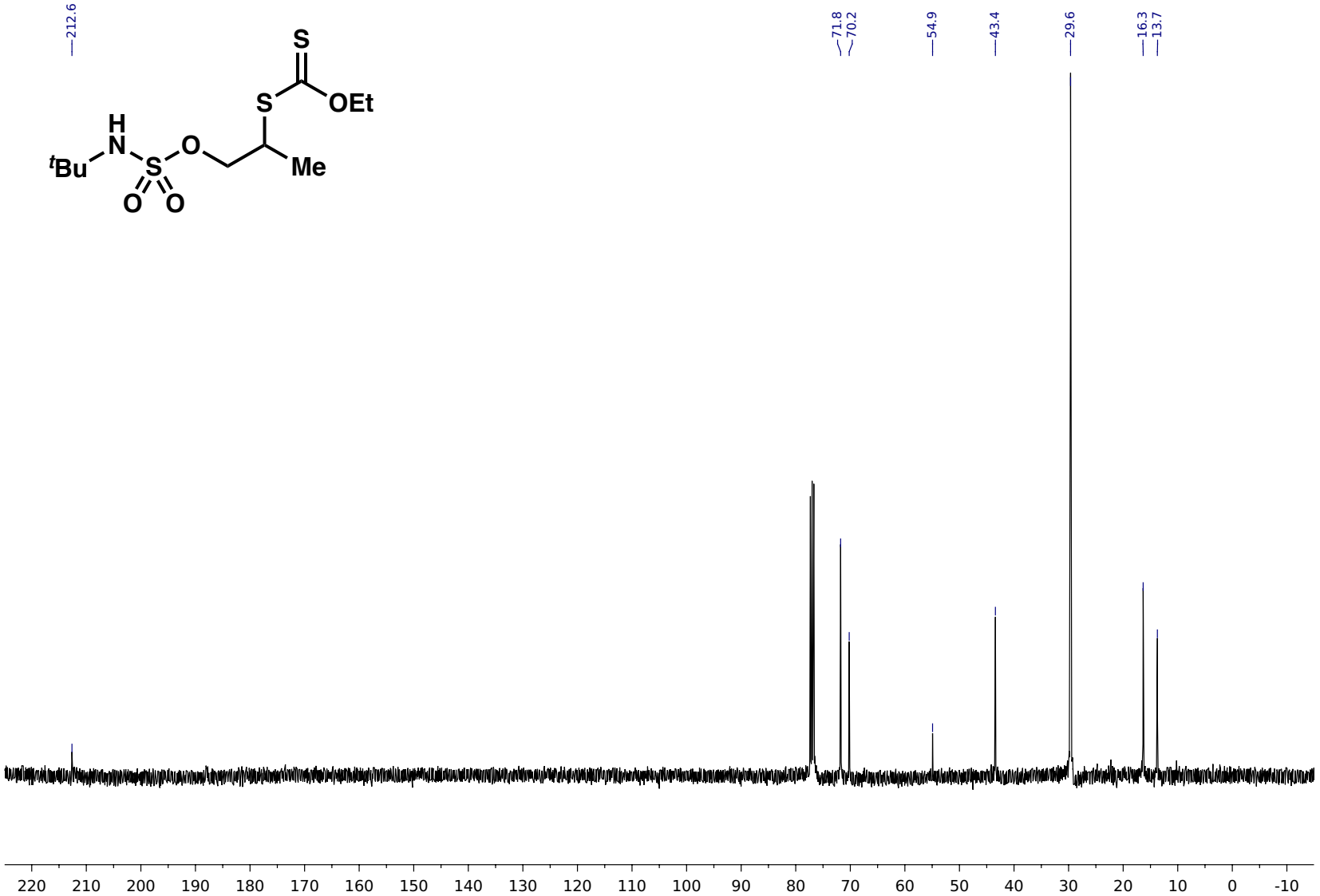
^{1}H NMR (400 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)propyl *tert*-butylsulfamate **(2n)**



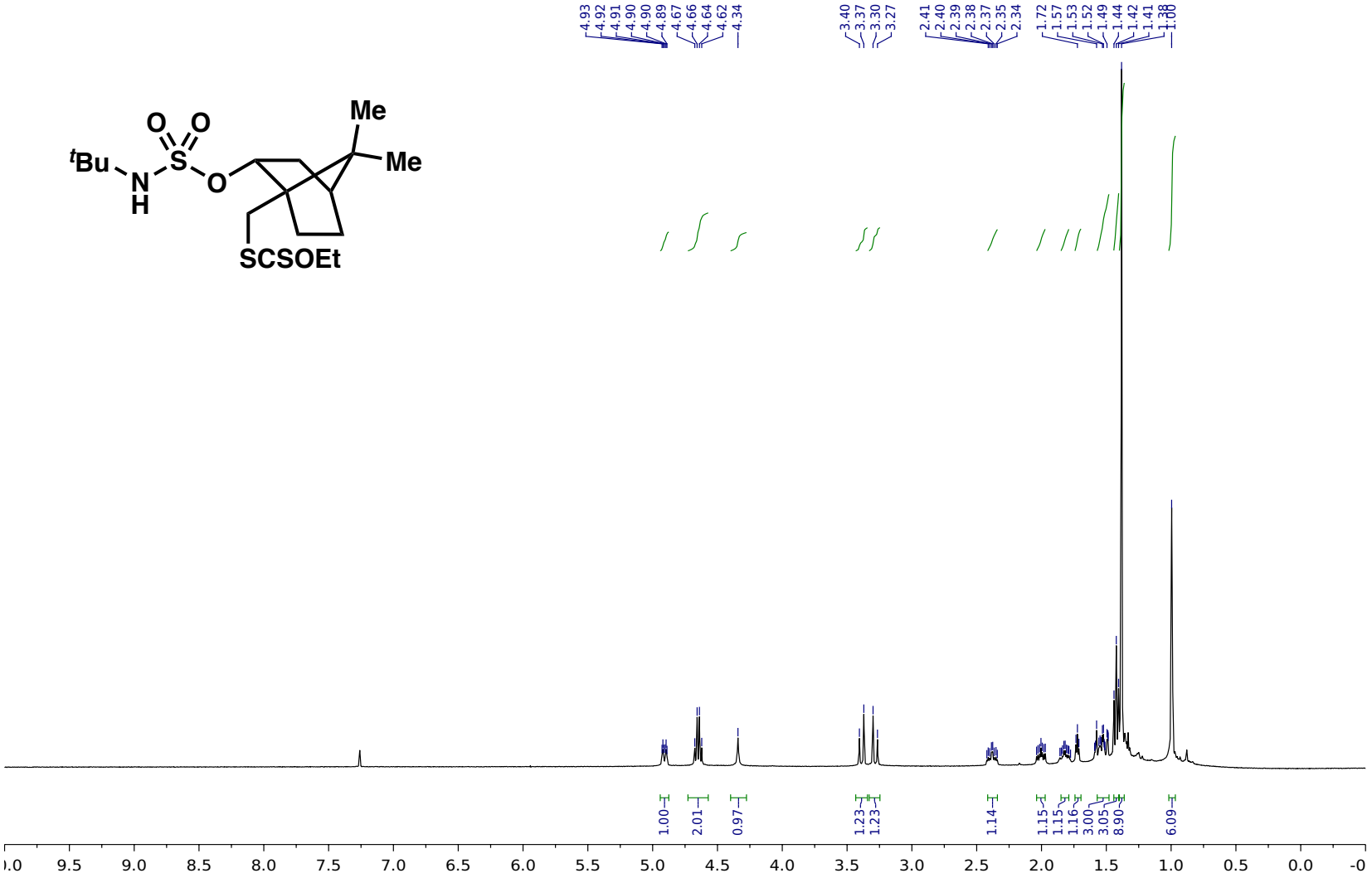
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)propyl *tert*-butylsulfamate **(2n)**



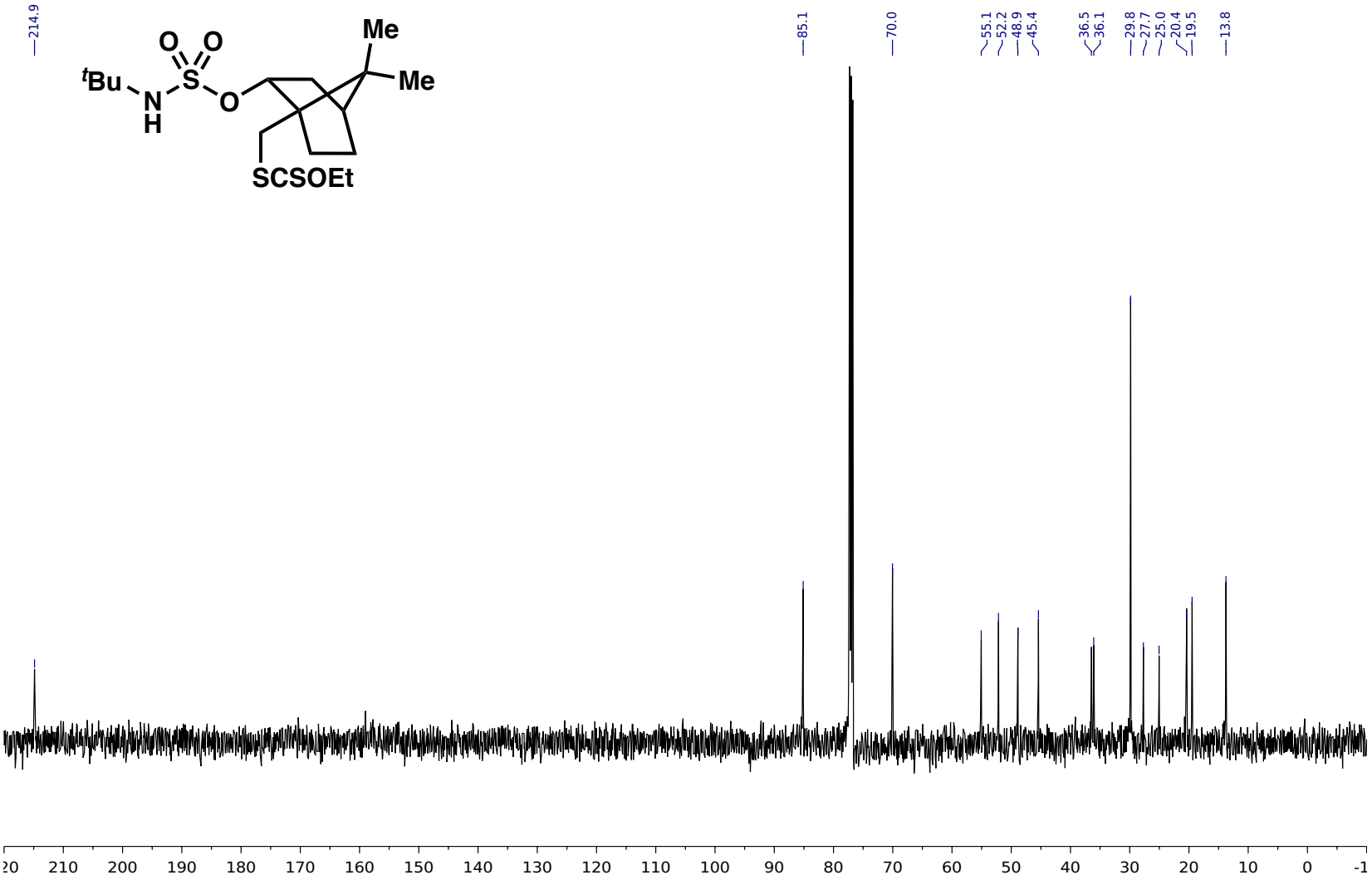
^{1}H NMR (400 MHz, $CDCl_3$) for 2-((ethoxycarbonothioyl)thio)propyl *tert*-butylsulfamate **(S4a)**



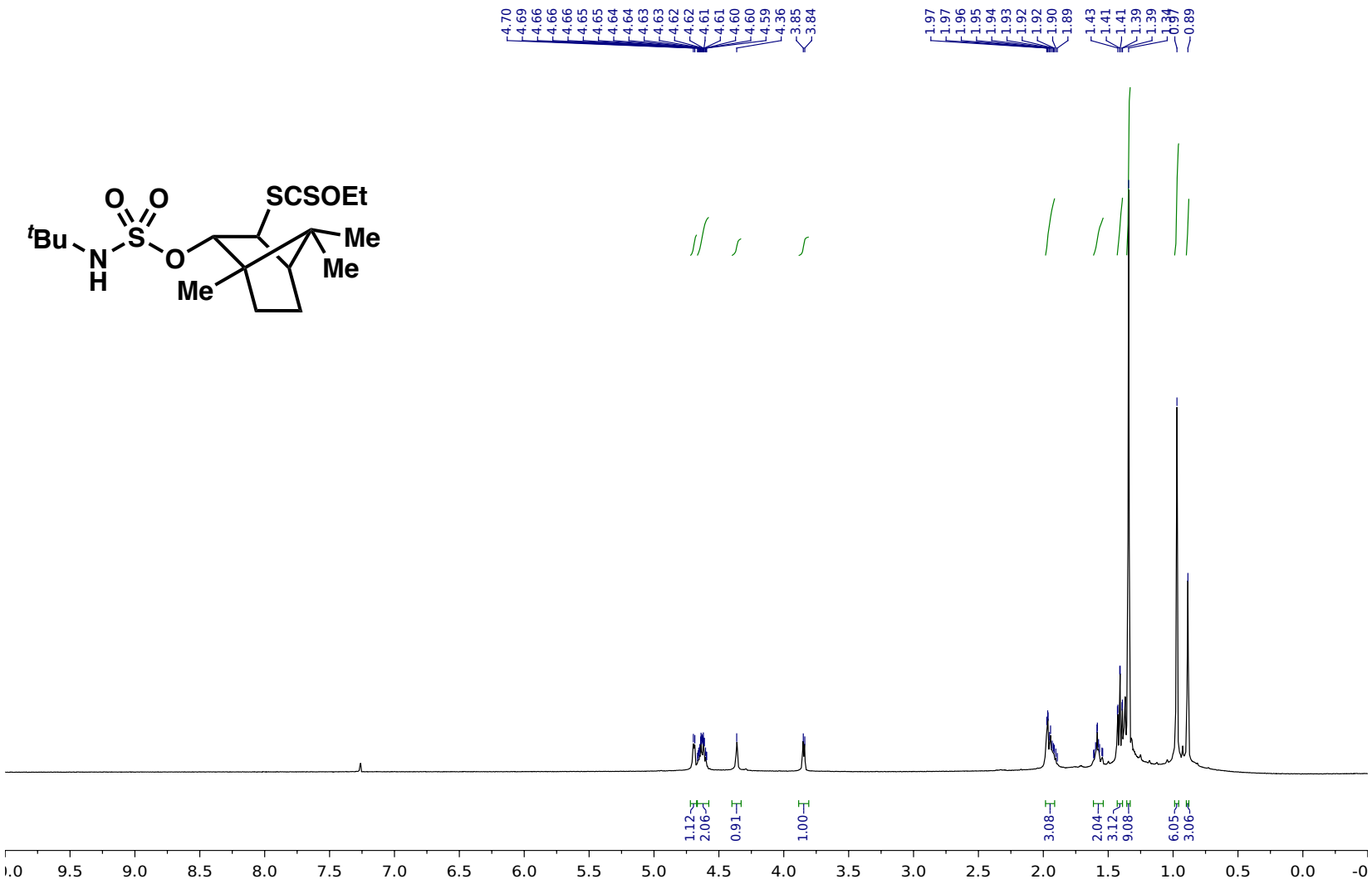
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 2-((ethoxycarbonothioyl)thio)propyl *tert*-butylsulfamate **(S4a)**



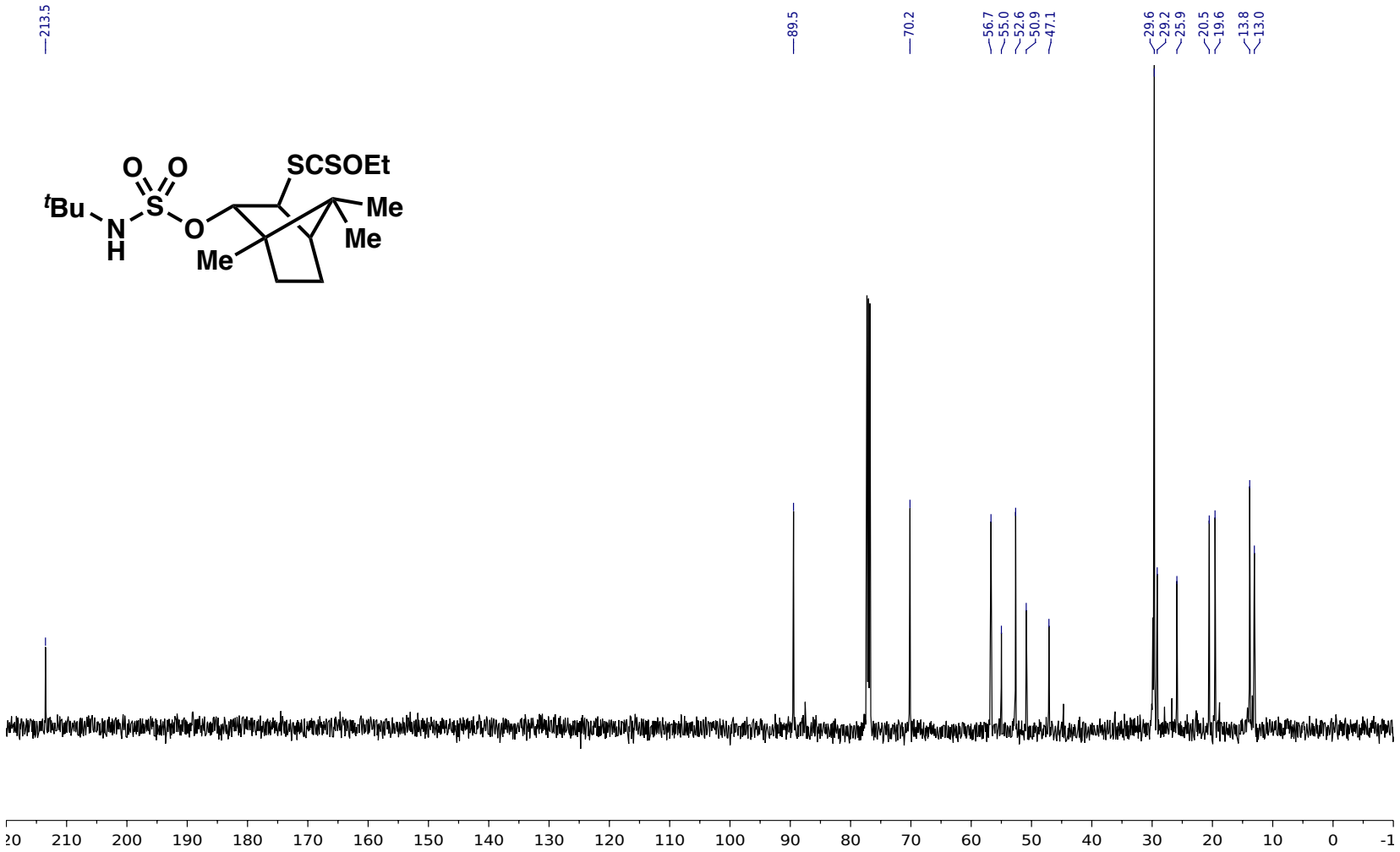
^{1}H NMR (400 MHz, $CDCl_3$) for (1*S*, 2*S*)-1-(((ethoxycarbonothioyl)thio)methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl *tert*-butylsulfamate **(2o)**



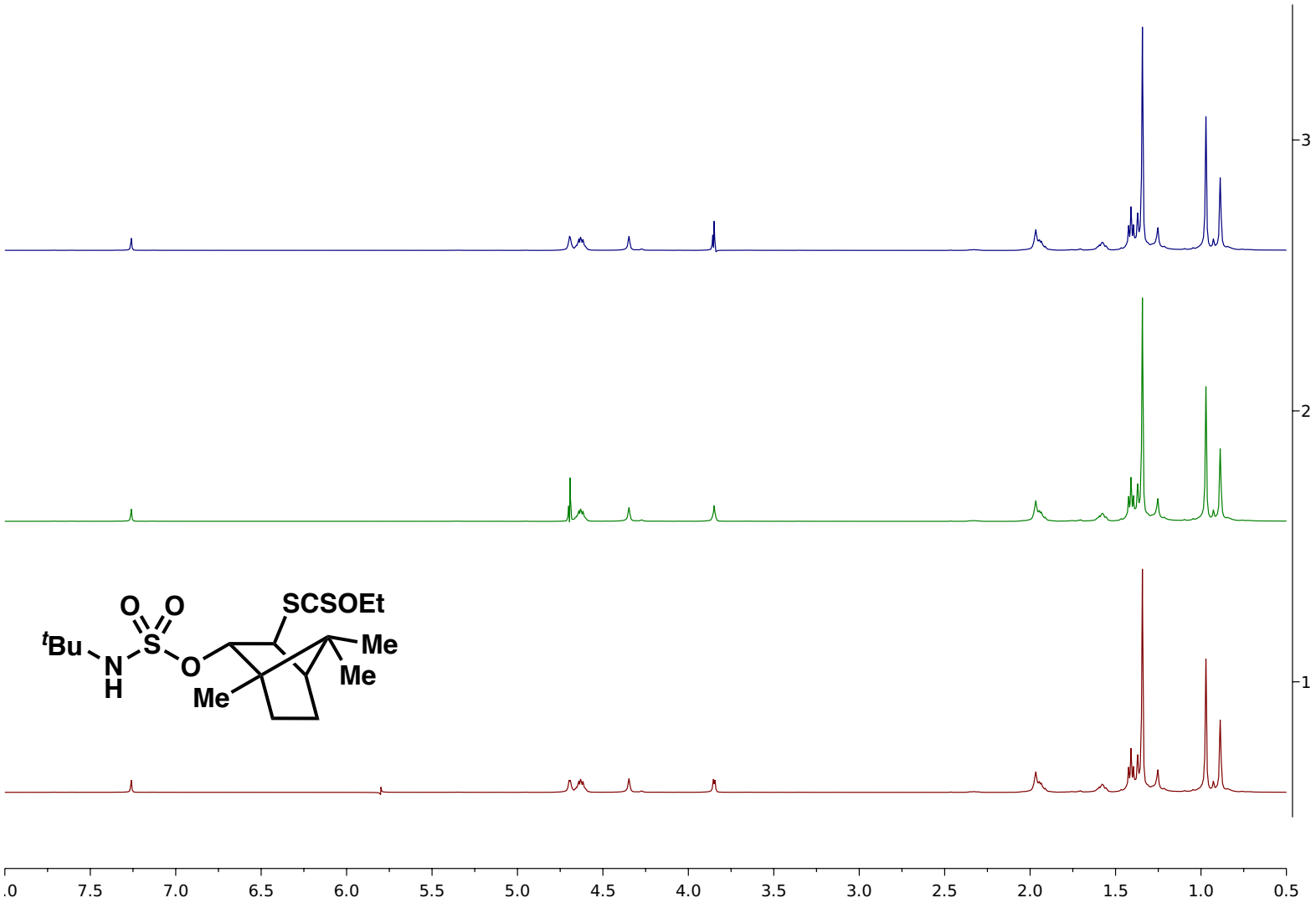
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for (1*S*, 2*R*)-1-(((ethoxycarbonothioyl)thio)methyl)-7,7-dimethylbicyclo[2.2.1]heptan-2-yl *tert*-butylsulfamate **(2o)**



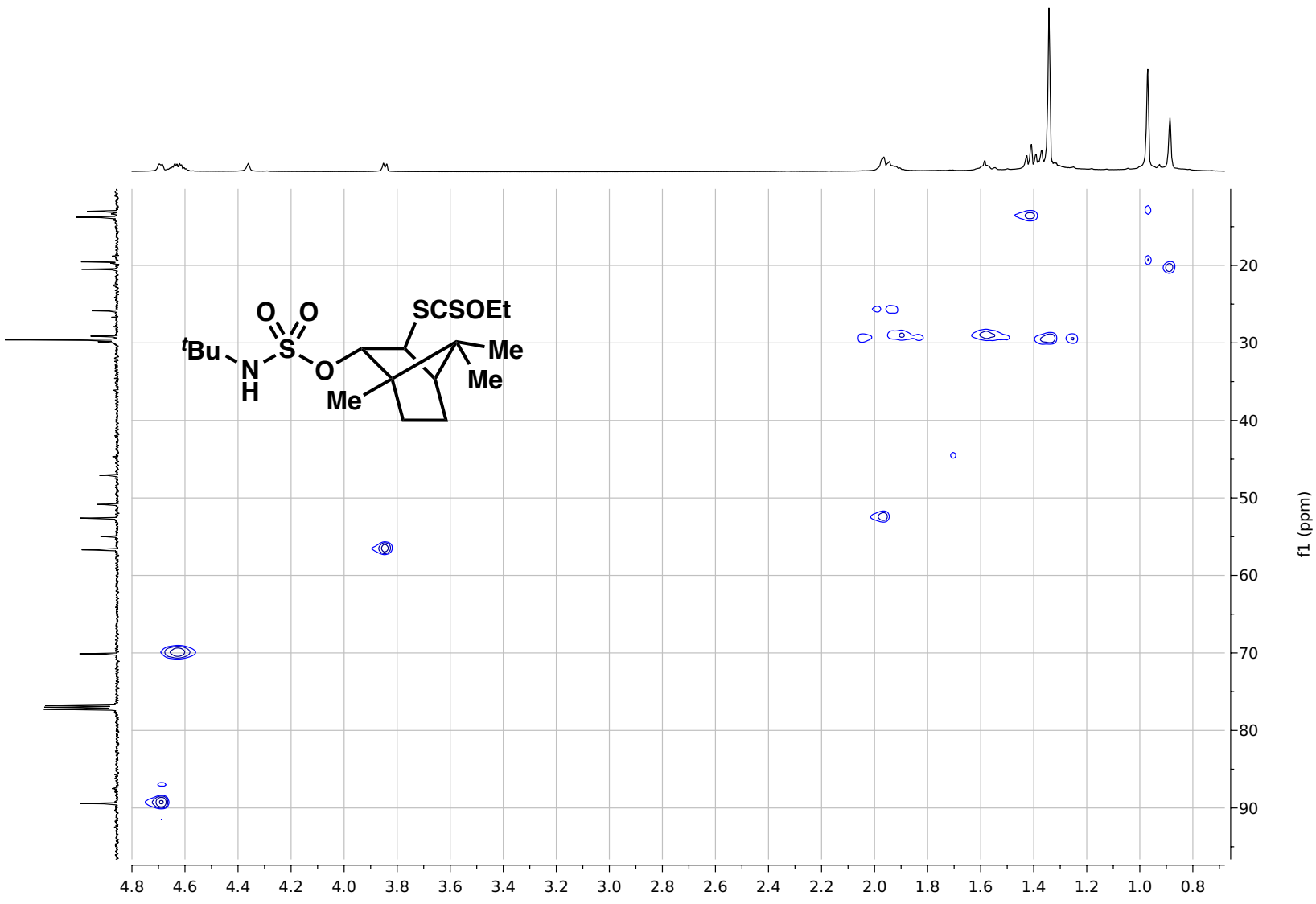
^{1}H NMR (400 MHz, $CDCl_3$) for (1*R*, 2*R,* 3*R*)-3-((ethoxycarbonothioyl)thio)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl *tert*-butylsulfamate **(S4b)**



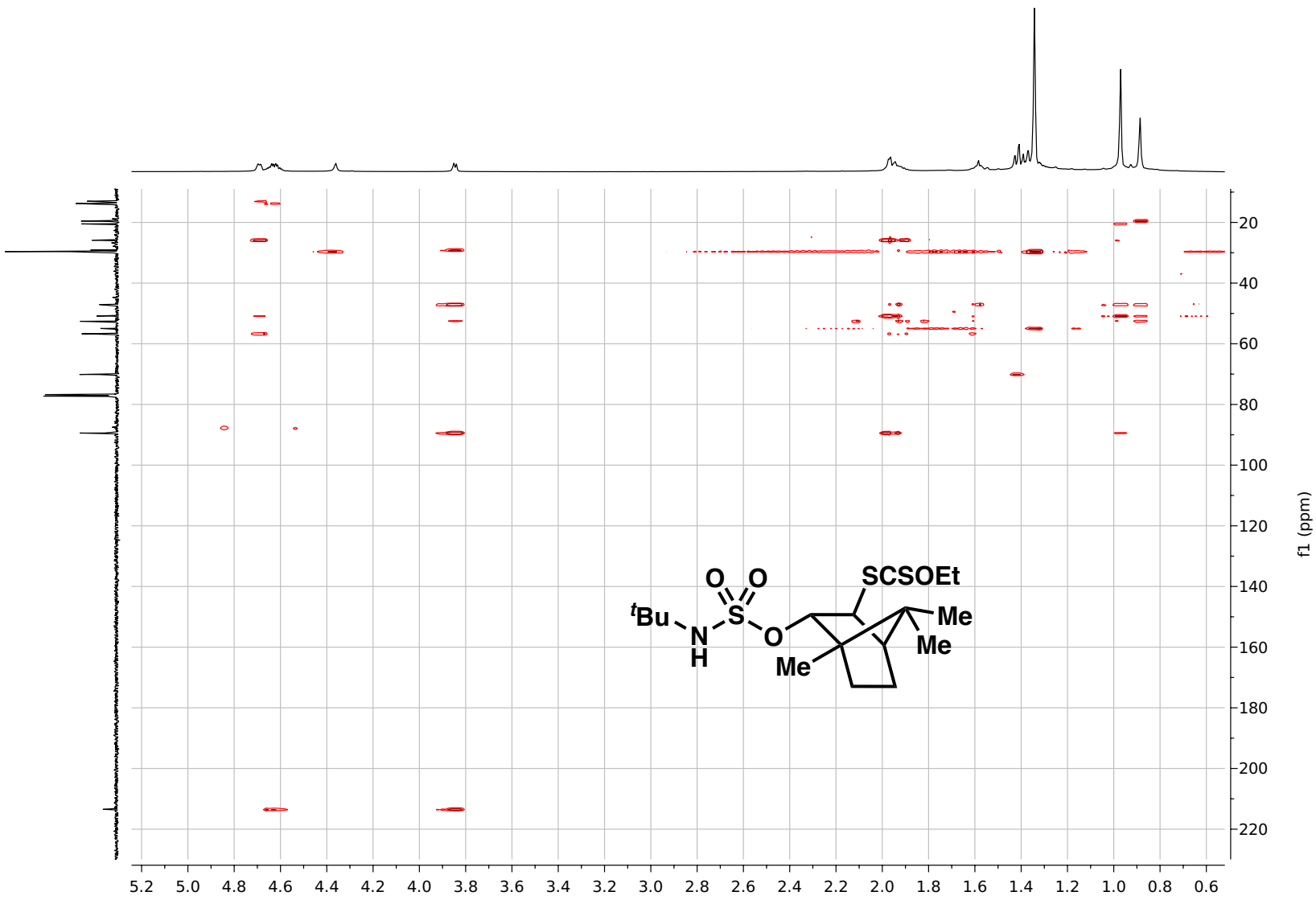
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for (1*S*, 2*R*, 3*R*)-3-(((ethoxycarbonothioyl)thio)methyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl *tert*-butylsulfamate **(S4b)**



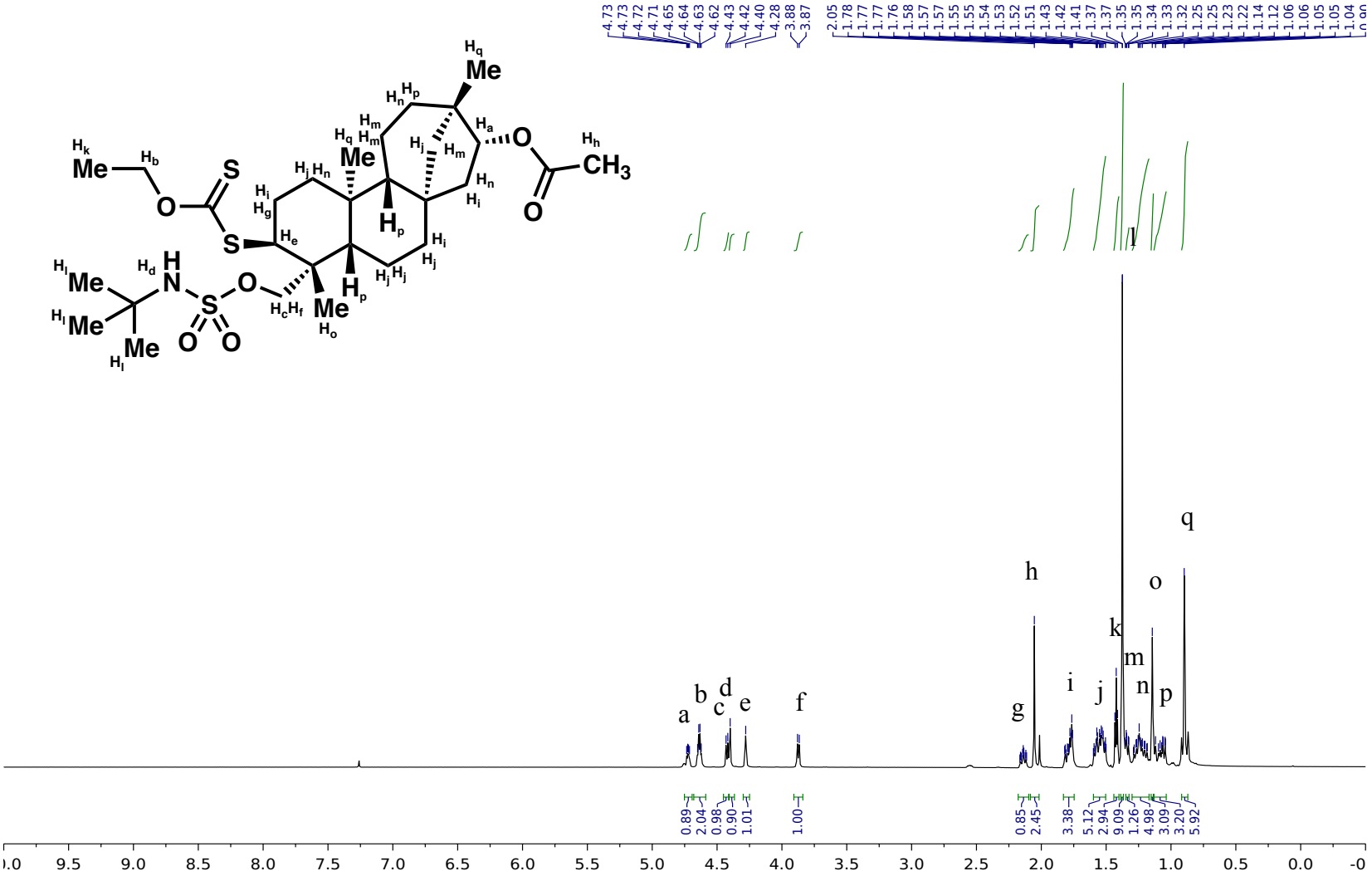
Homonuclear decoupling of **S4b** [Bottom: Control, Middle: Irradiation @ 4.9 ppm, Top: irradiation @ 3.85 ppm]


O
O
S
O
tBu
N
H
SCSOEt
Me
Me
Me
f1 (ppm)
20
30
40
50
60
70
80
90
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8

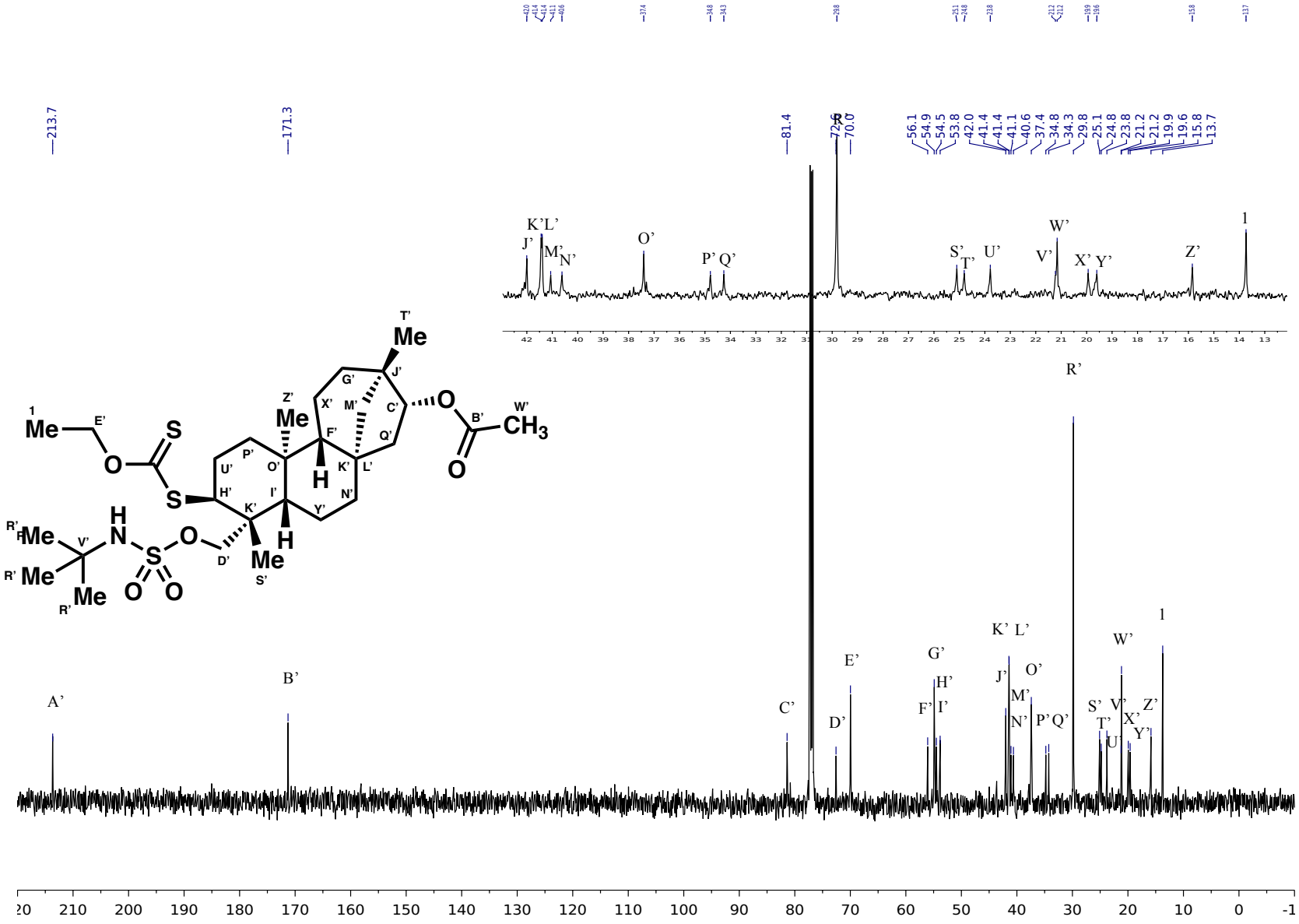
HMQC of **S4b**



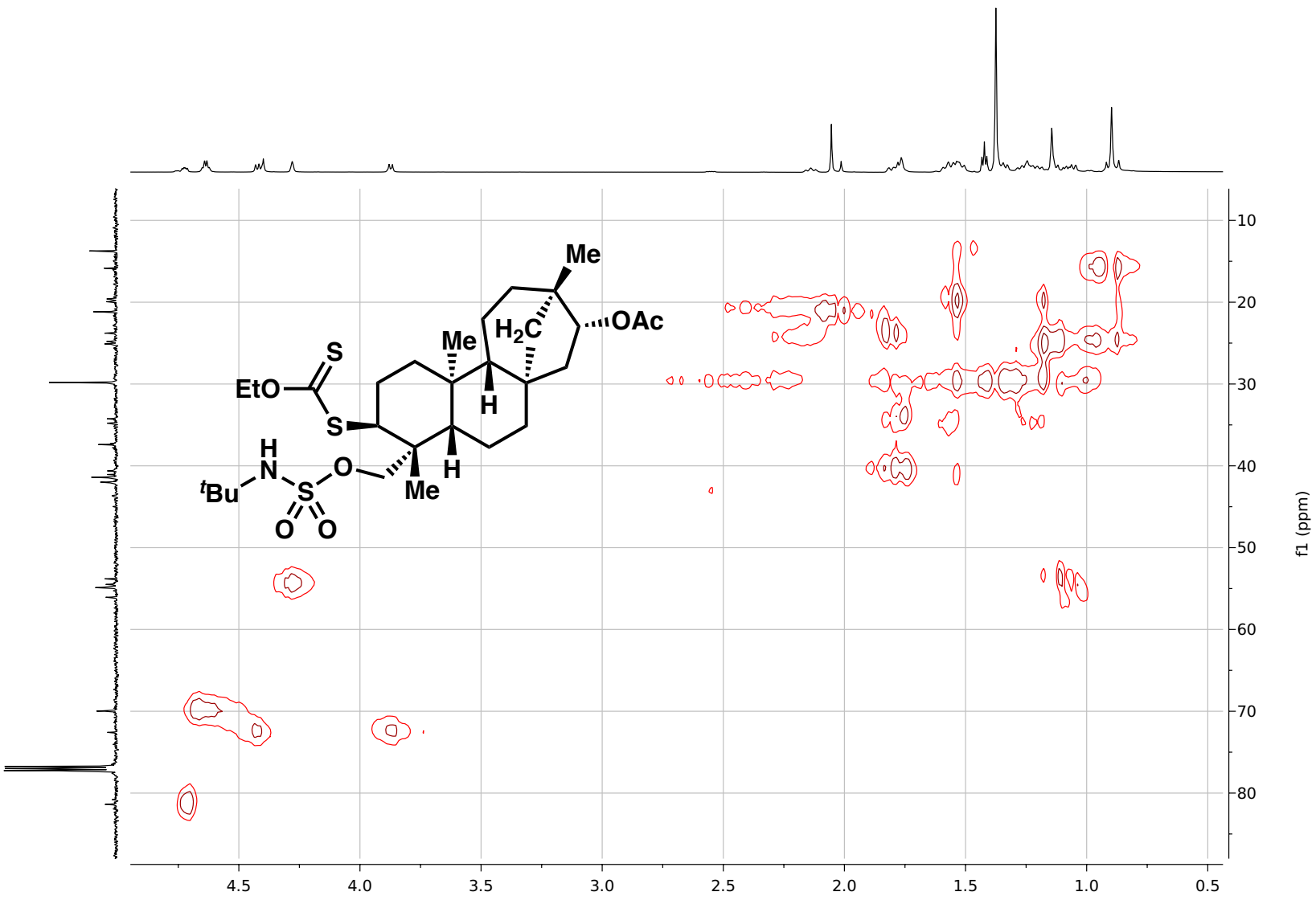
HMBC (8 Hz) of **S4b**



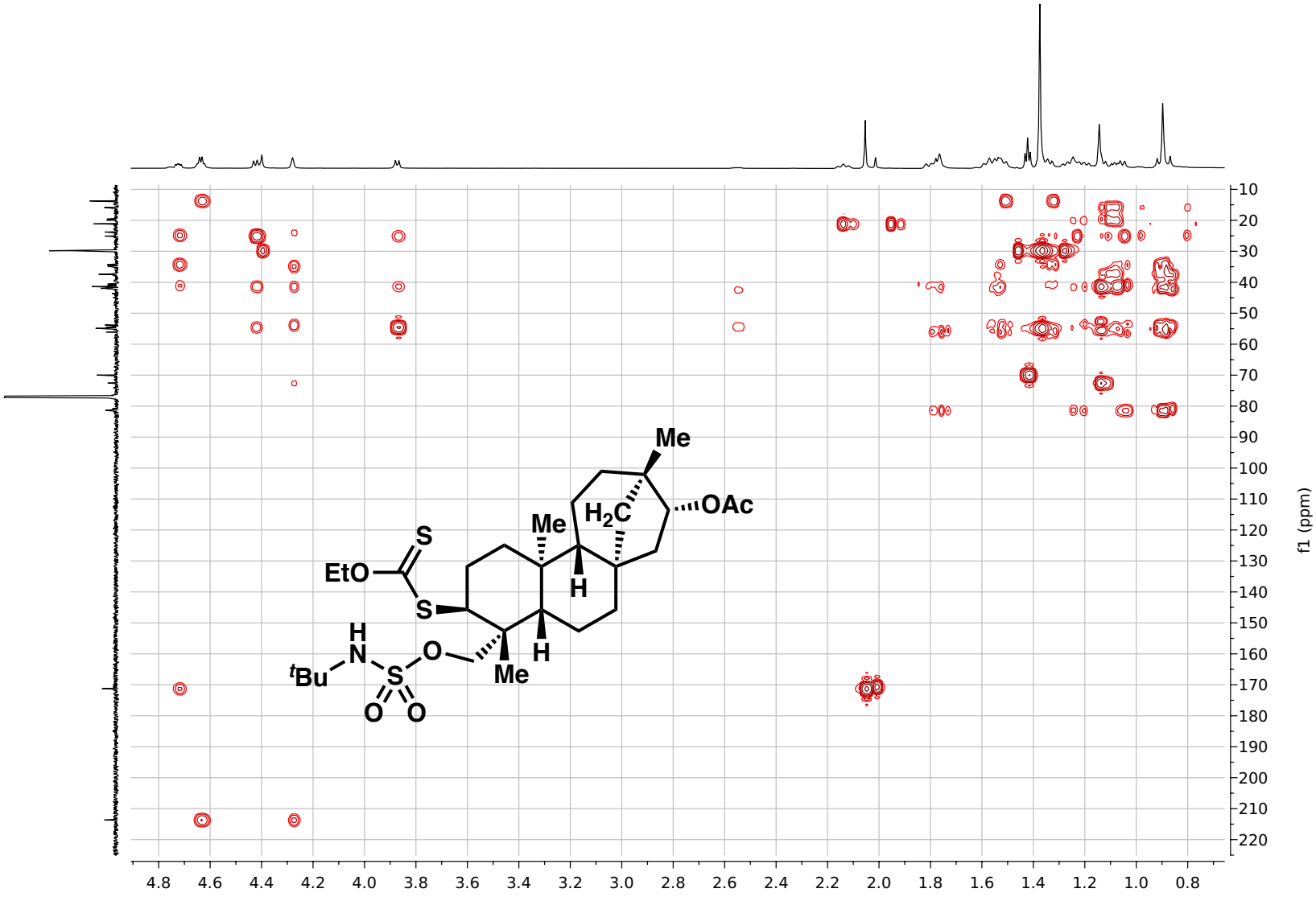
^{1}H NMR (700 MHz, $CDCl_3$) for (3*S*,4*R*,4a*S*,6a*S*,8*R*,9*R*,11a*R*,11b*S*)-4-(((*N*-(*tert*-butyl)sulfamoyl)oxy)methyl)-3-((ethoxycarbonothioyl)thio)-4,9,11b-trimethyltetradecahydro-6a,9-methanocyclohepta[*a*]naphthalen-8-yl acetate **(2p)**



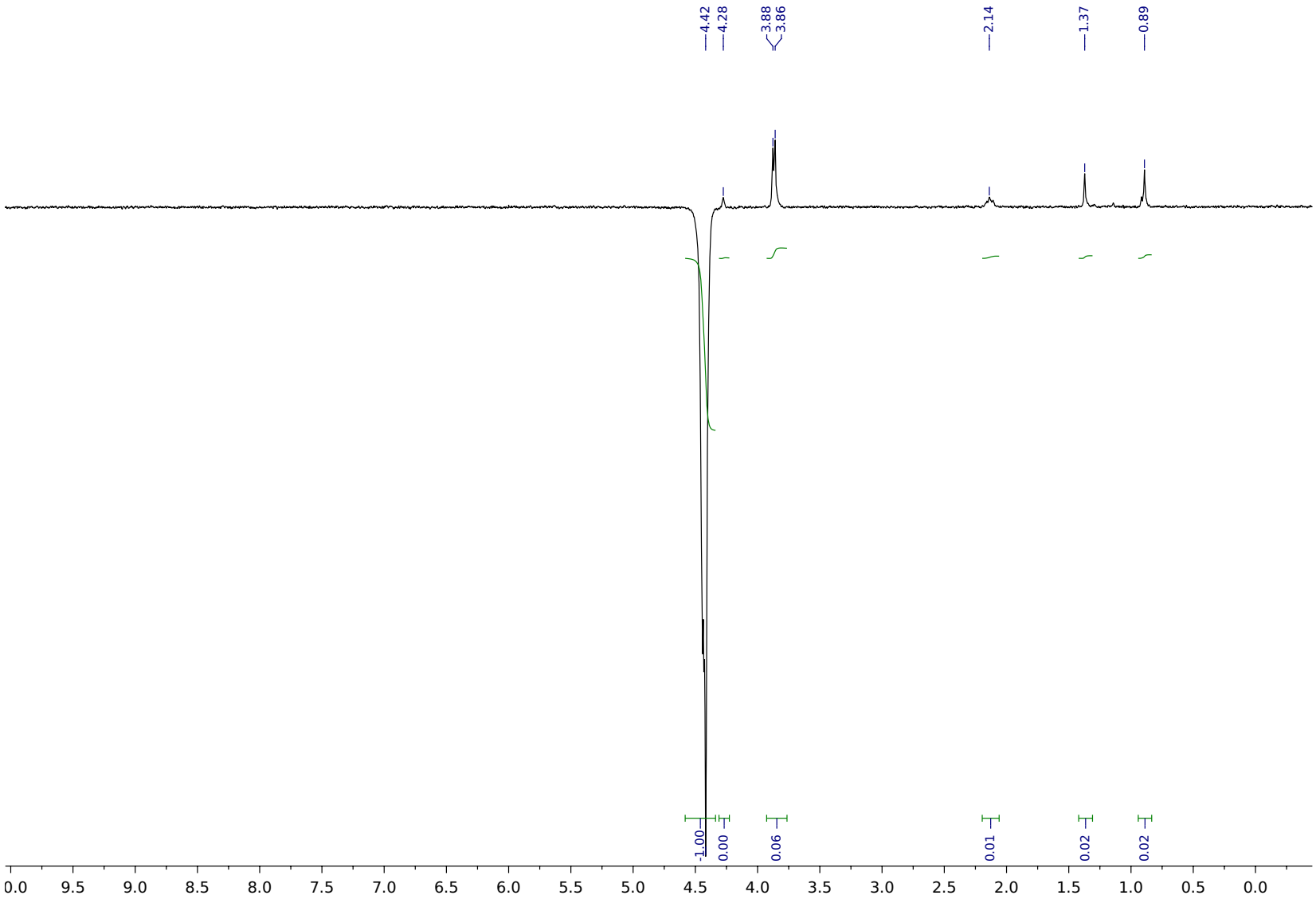
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for (3*S*,4*R*,4a*S*,6a*S*,8*R*,9*R*,11a*R*,11b*S*)-4-(((*N*-(*tert*-butyl)sulfamoyl)oxy)methyl)-3-((ethoxycarbonothioyl)thio)-4,9,11b-trimethyltetradecahydro-6a,9-methanocyclohepta[*a*]naphthalen-8-yl acetate **(2p)**


Me
H2C
OAc
Me
EtO
S
S
H
N
O
tBu
S
O
O
Me
H
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
10
20
30
40
50
60
70
80
f1 (ppm)

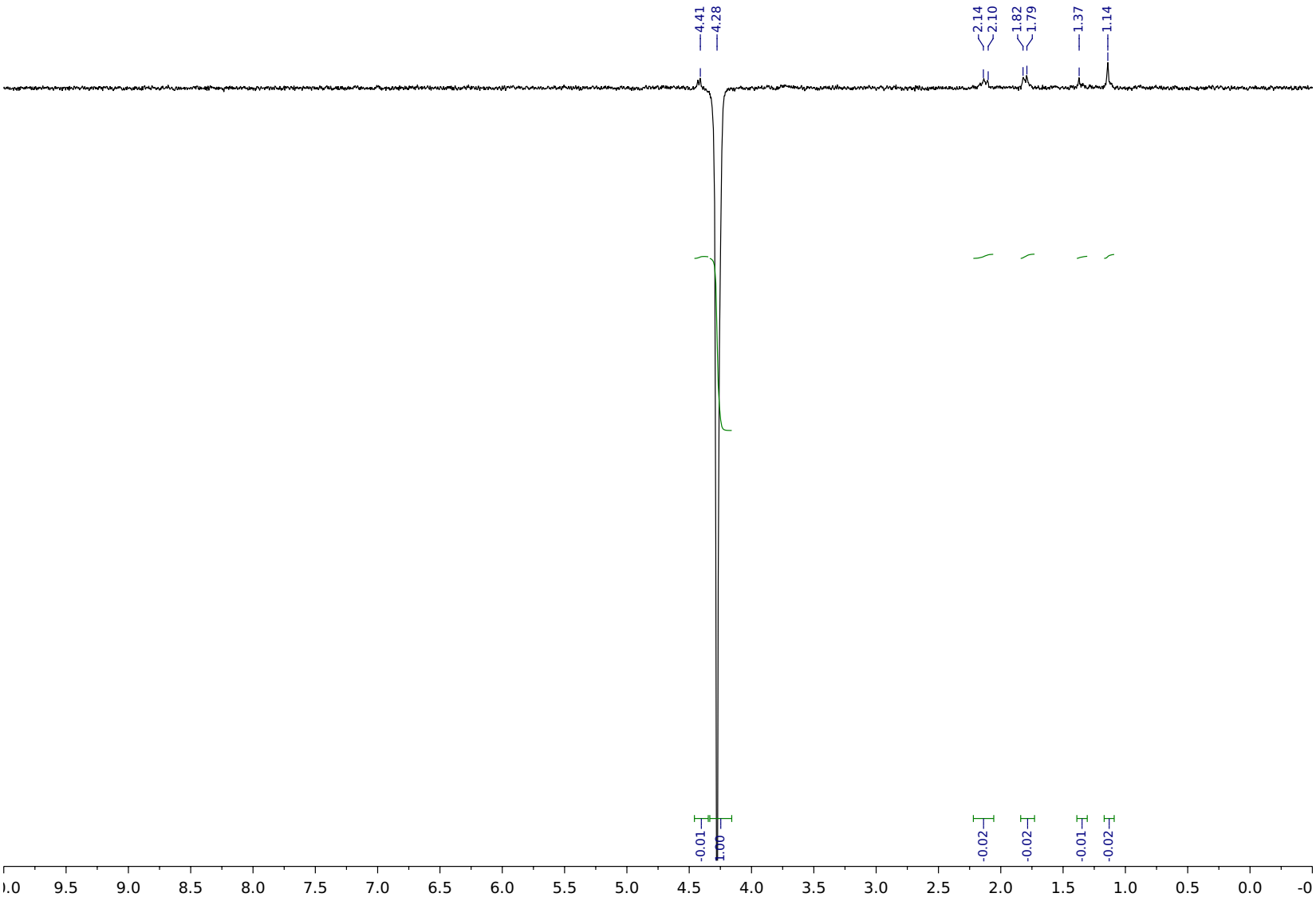
HMQC of **2p**



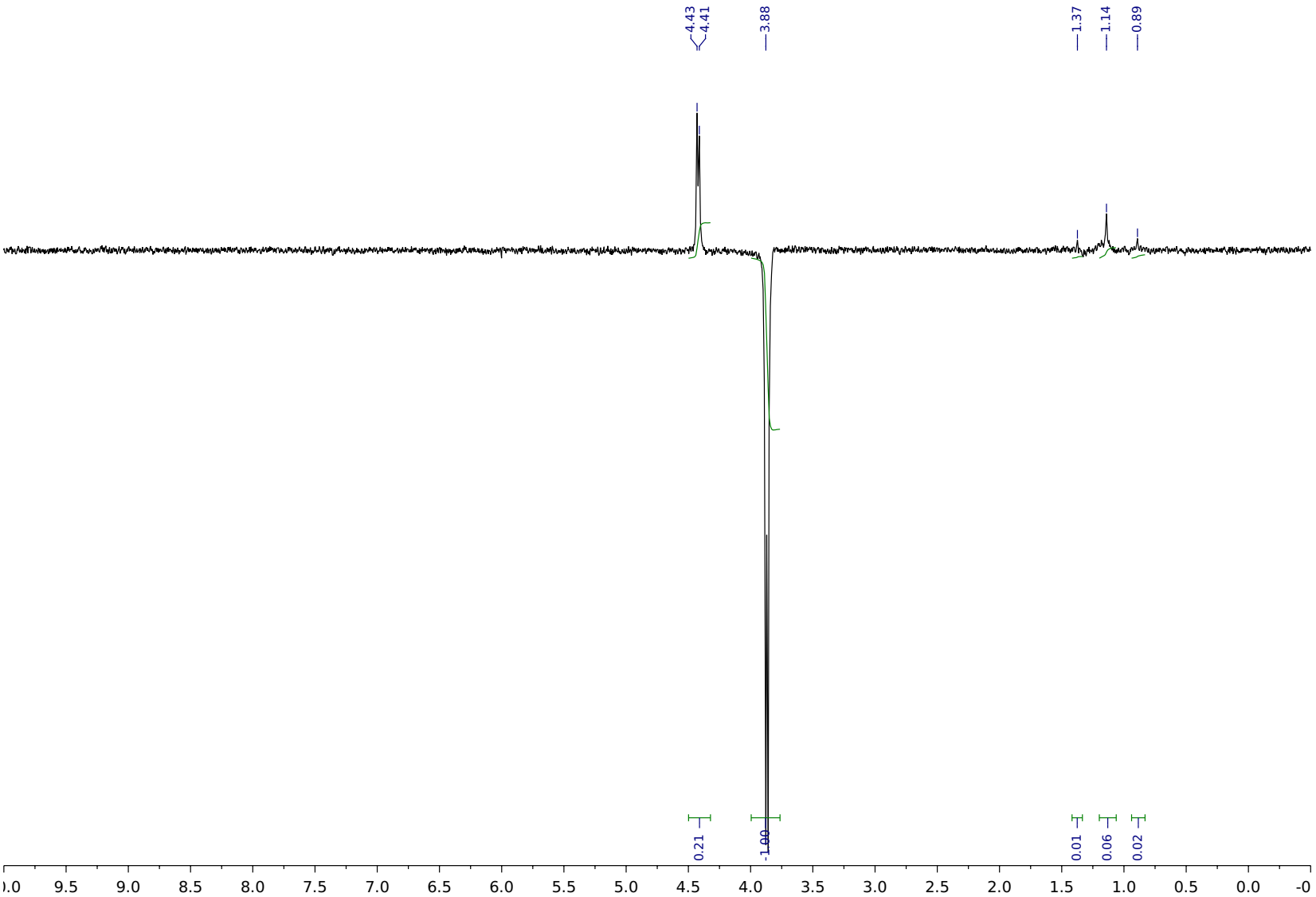
HMBC (8 Hz) of **2p**



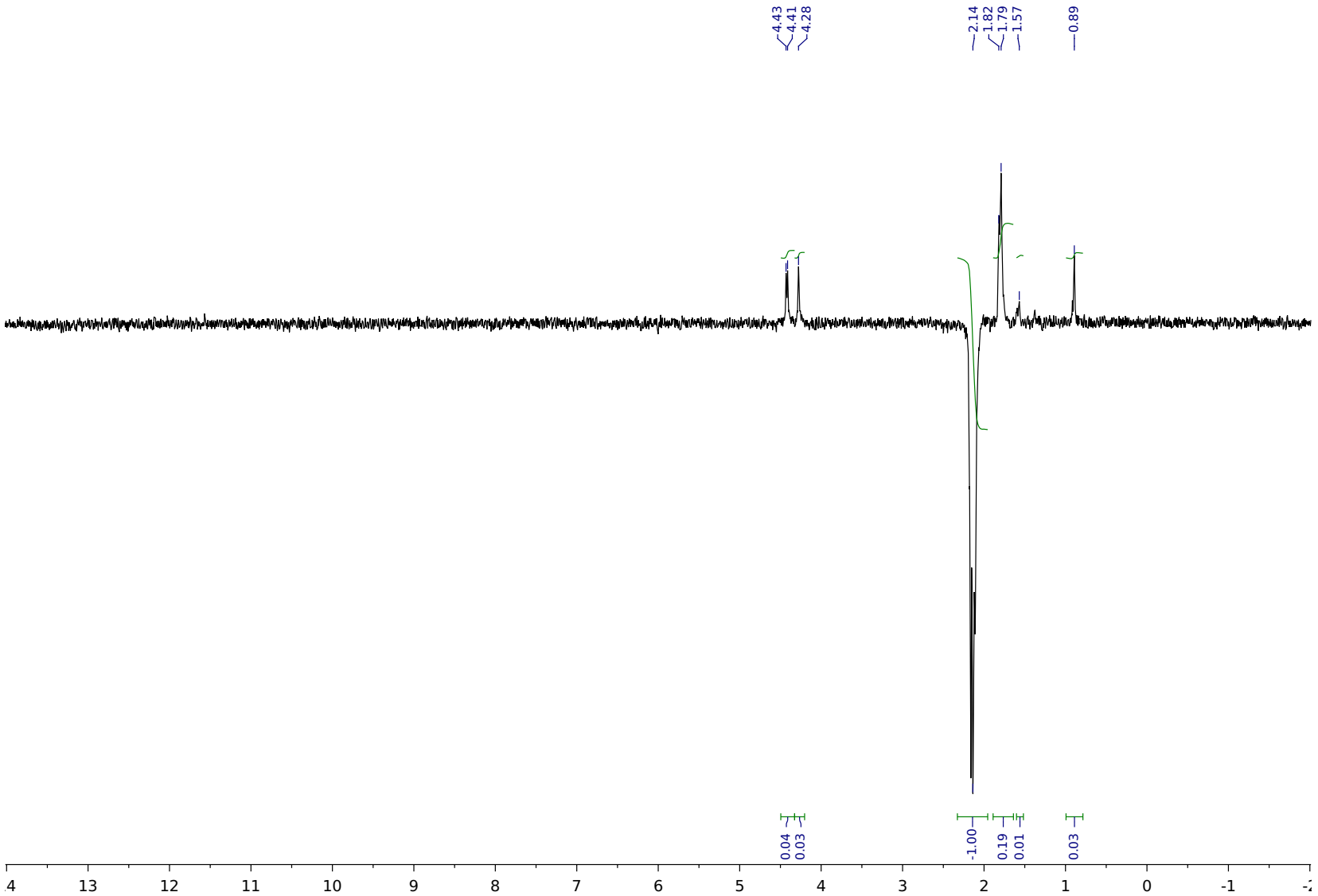
1D-^{1}H NOESY of **2p** [Excitation @ 4.42 ppm, mixing time = 500 ms]



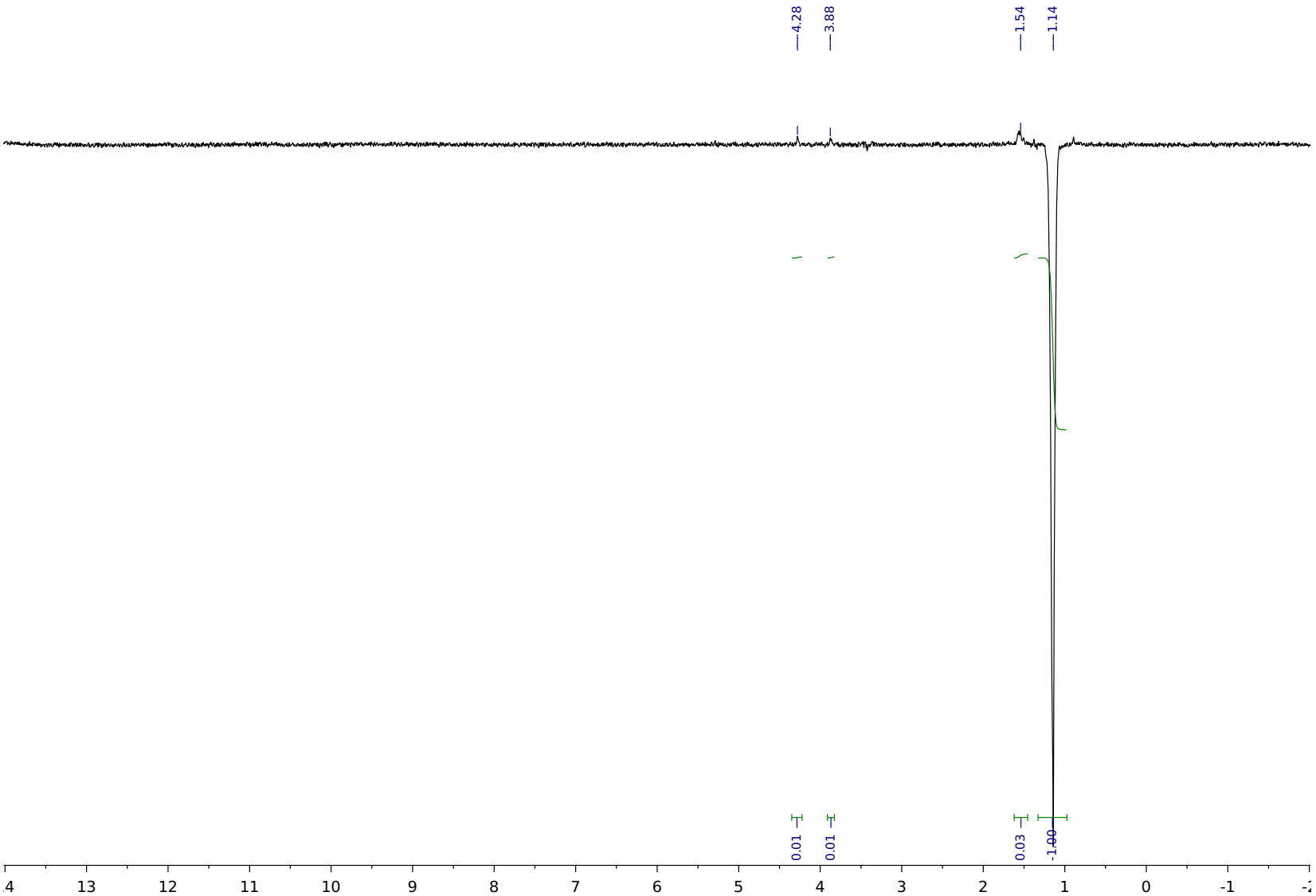
1D-^{1}H NOESY of **2p** [Excitation @ 4.2 ppm, mixing time = 500 ms]



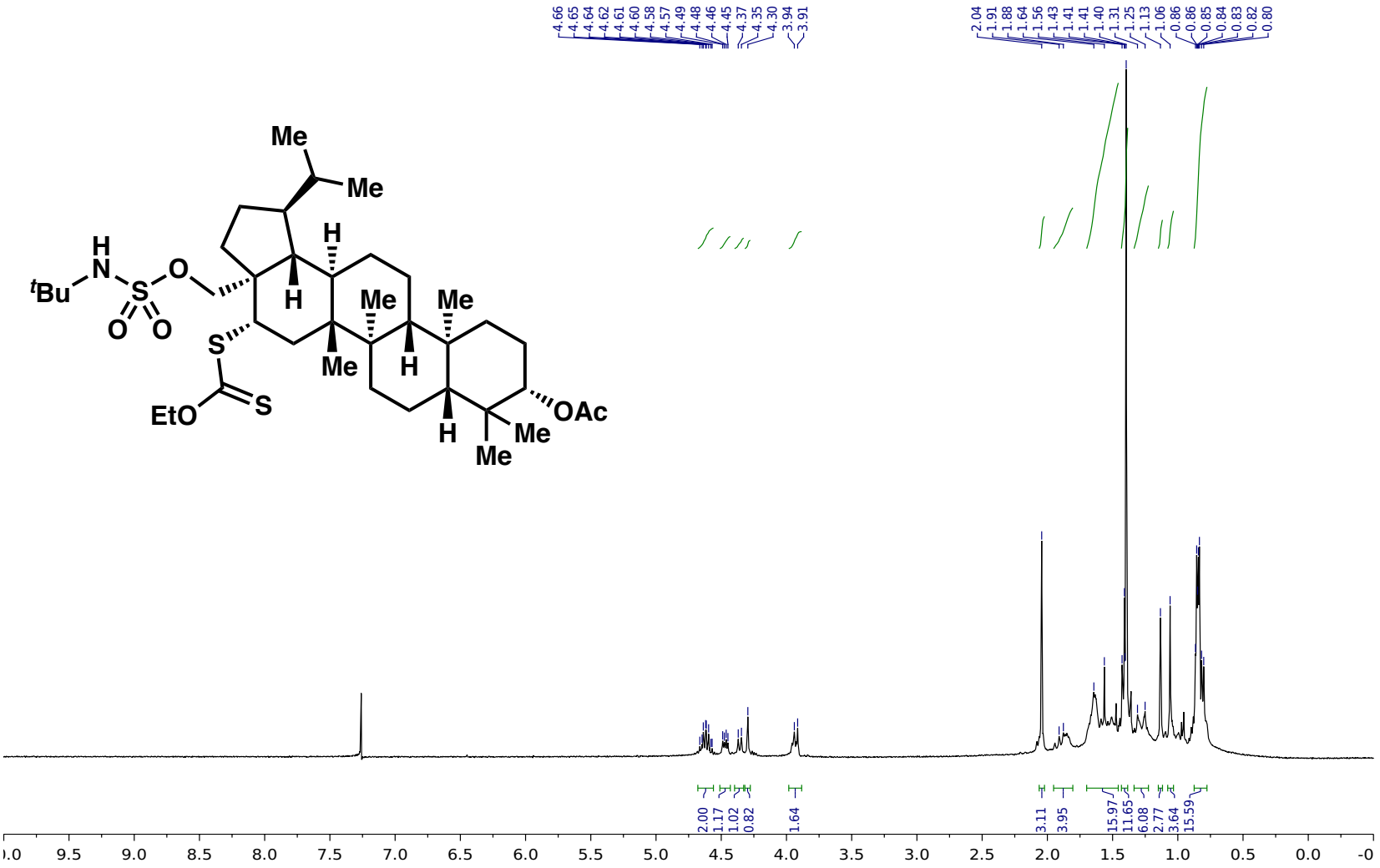
1D-^{1}H NOESY of **2p** [Excitation @ 3.8 ppm, mixing time = 500 ms]



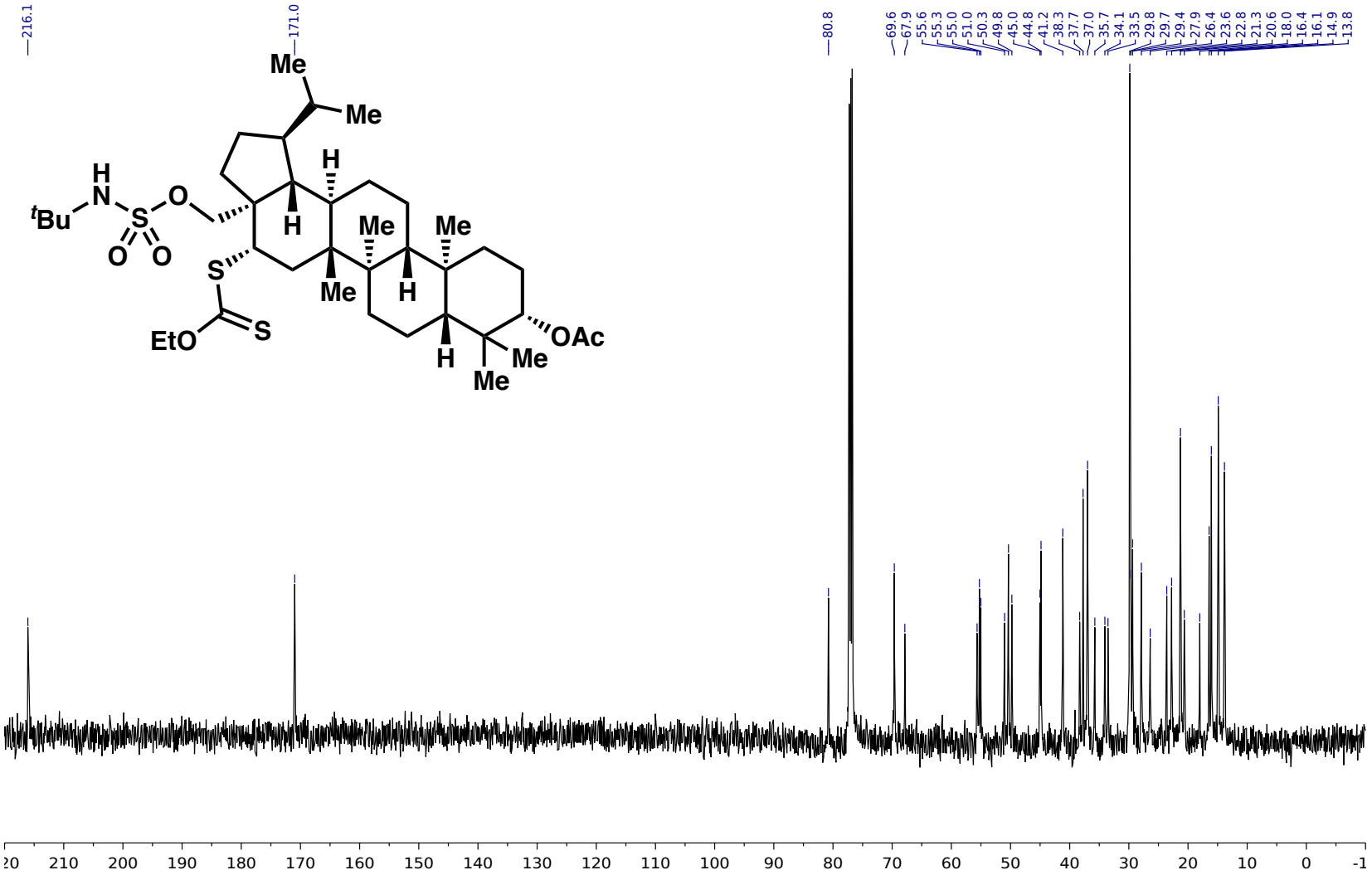
1D-^{1}H NOESY of **2p** [Excitation @ 2.12 ppm, mixing time = 500 ms]



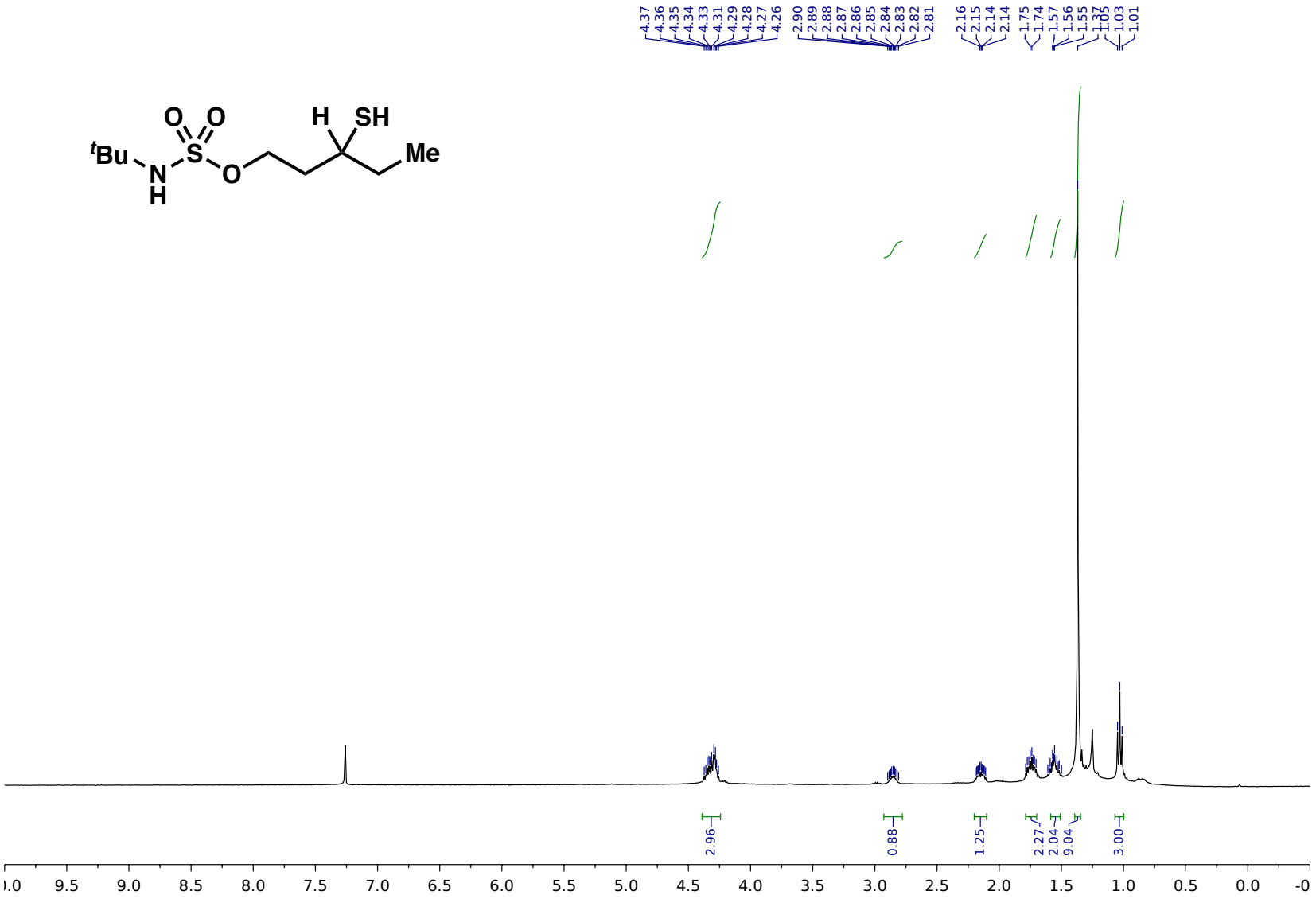
1D-^{1}H NOESY of **2p** [Excitation @ 1.14 ppm, mixing time = 500 ms]



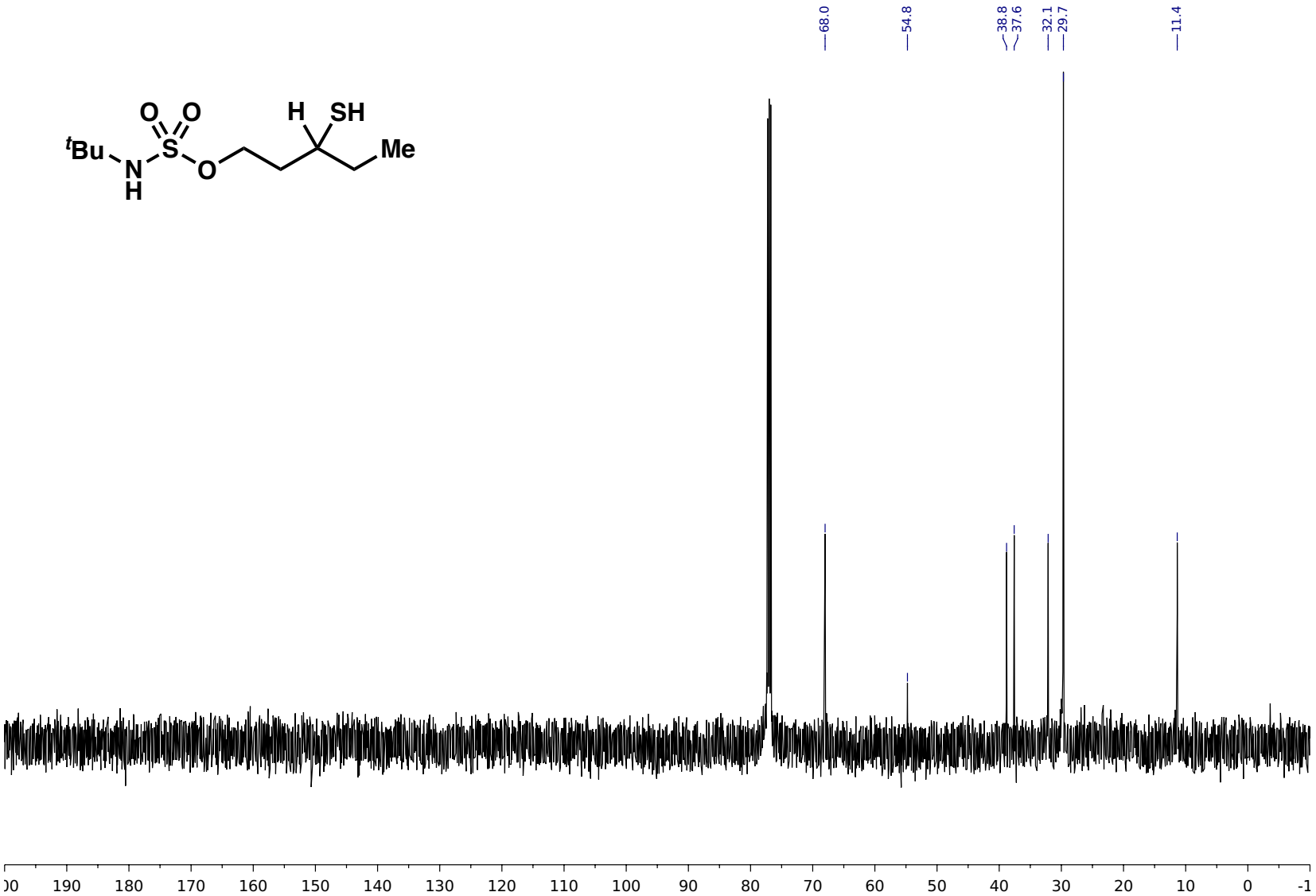
^{1}H NMR (400 MHz, $CDCl_3$) for (1*R*,3a*S*,5a*S*,5b*S*,7a*S*,9*R*,11a*S*,11b*S*,13a*S*,13b*S*)-3a-(((*N*-(*tert*-butyl)sulfamoyl)oxy)methyl)-3-((ethoxycarbonothioyl)thio)-1-isopropyl-5a,5b,8,8,11a-pentamethylicosahydro-1*H*-cyclopenta[*a*]chrysen-9-yl acetate **(2q)**



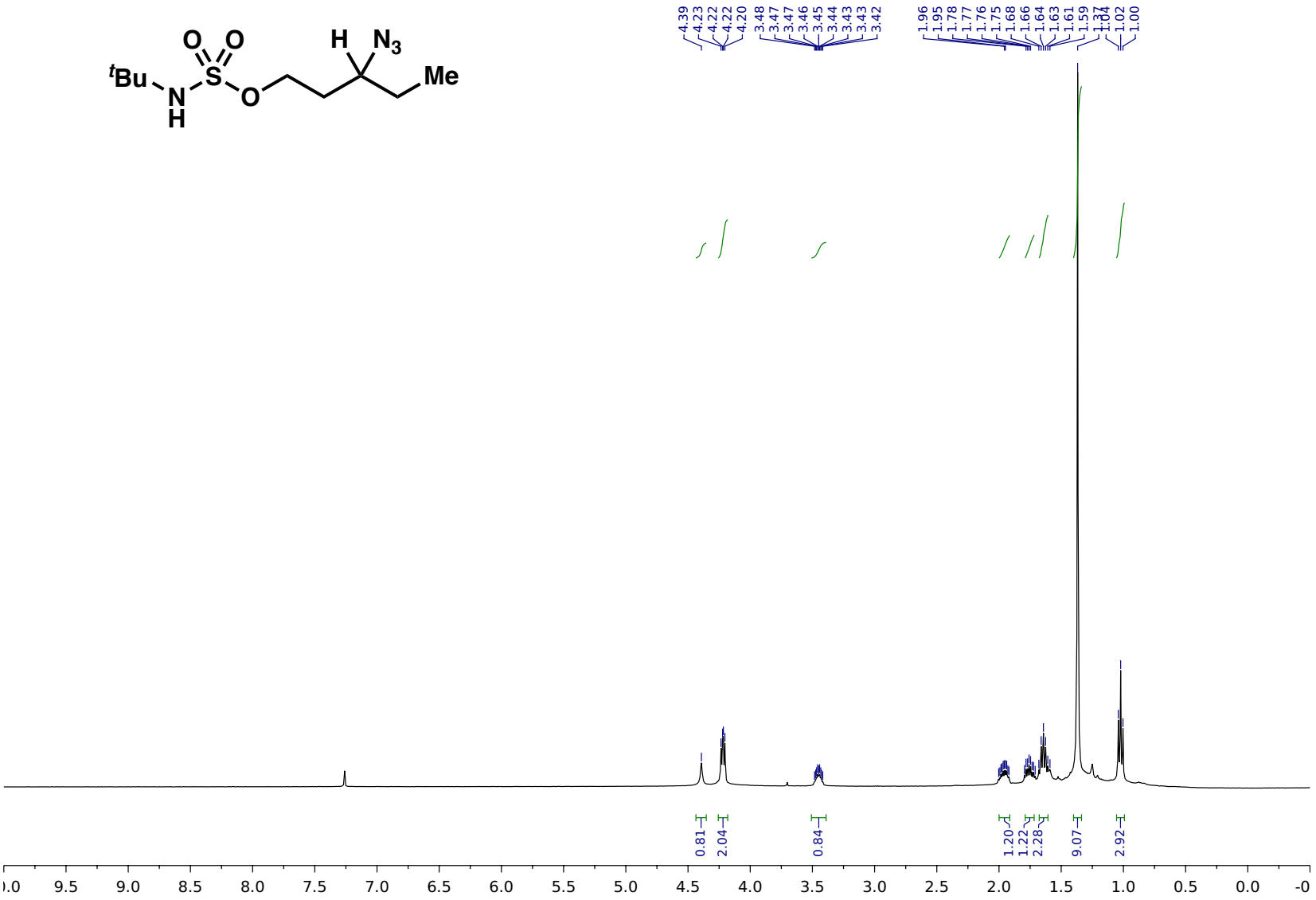
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for (1*R*,3a*S*,5a*S*,5b*S*,7a*S*,9*R*,11a*S*,11b*S*,13a*S*,13b*S*)-3a-(((*N*-(*tert*-butyl)sulfamoyl)oxy)methyl)-3-((ethoxycarbonothioyl)thio)-1-isopropyl-5a,5b,8,8,11a-pentamethylicosahydro-1*H*-cyclopenta[*a*]chrysen-9-yl acetate **(2q)**



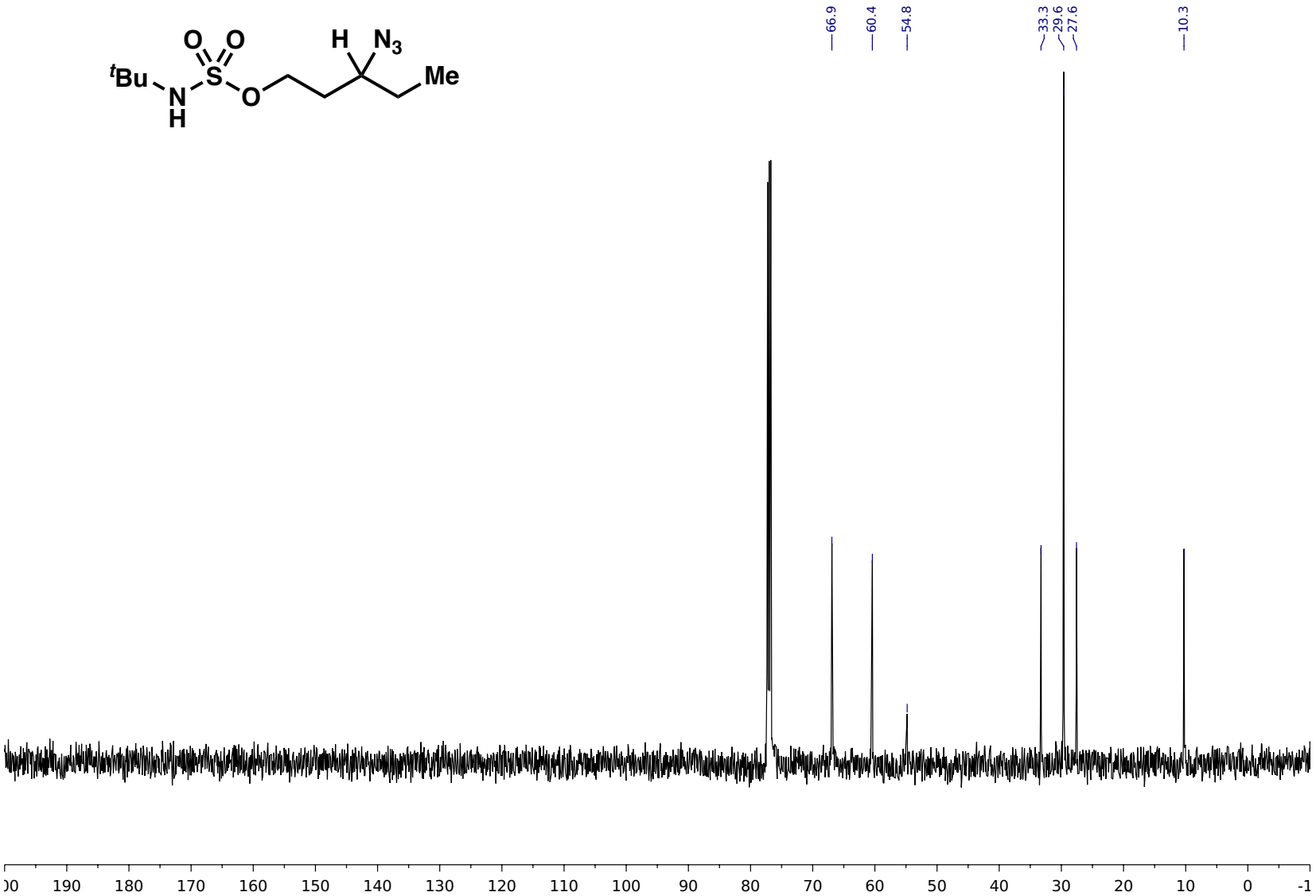
^{1}H NMR (400 MHz, $CDCl_3$) for 3-mercapto pentyl *tert*-butylsulfamate **(7)**



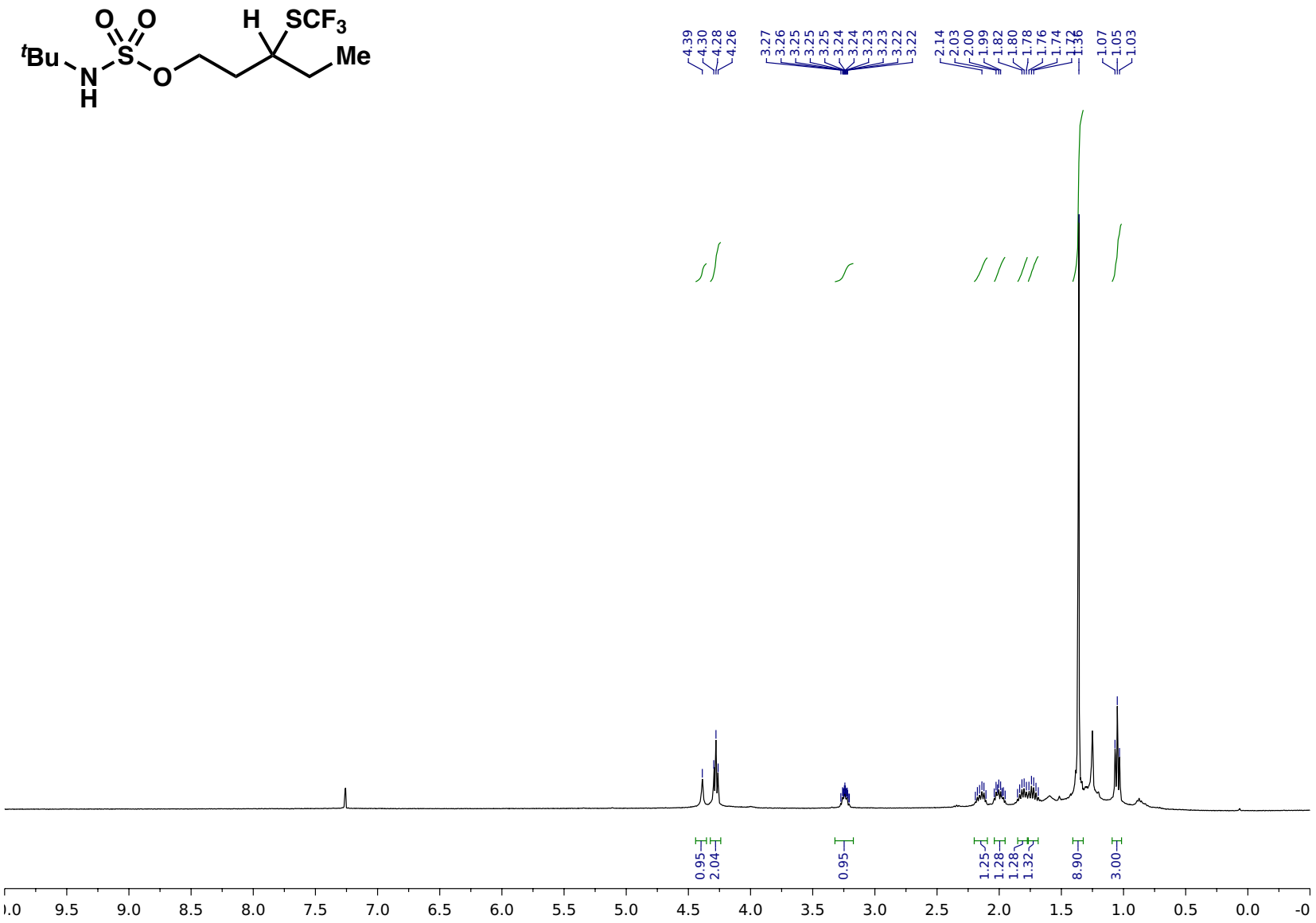
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)propyl *tert*-butylsulfamate **(7)**



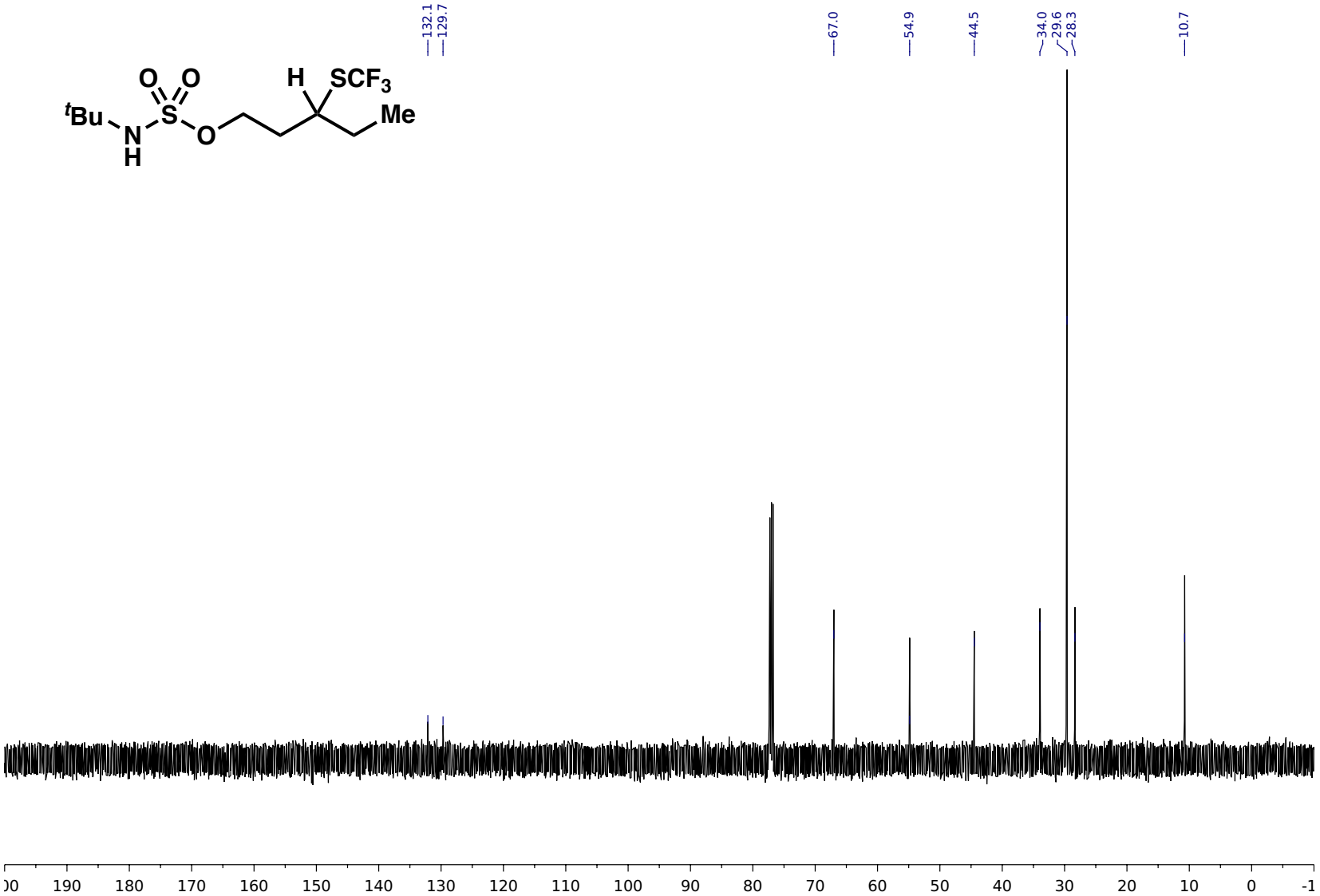
^{1}H NMR (400 MHz, $CDCl_3$) for 3-azido pentyl *tert*-butylsulfamate **(8)**



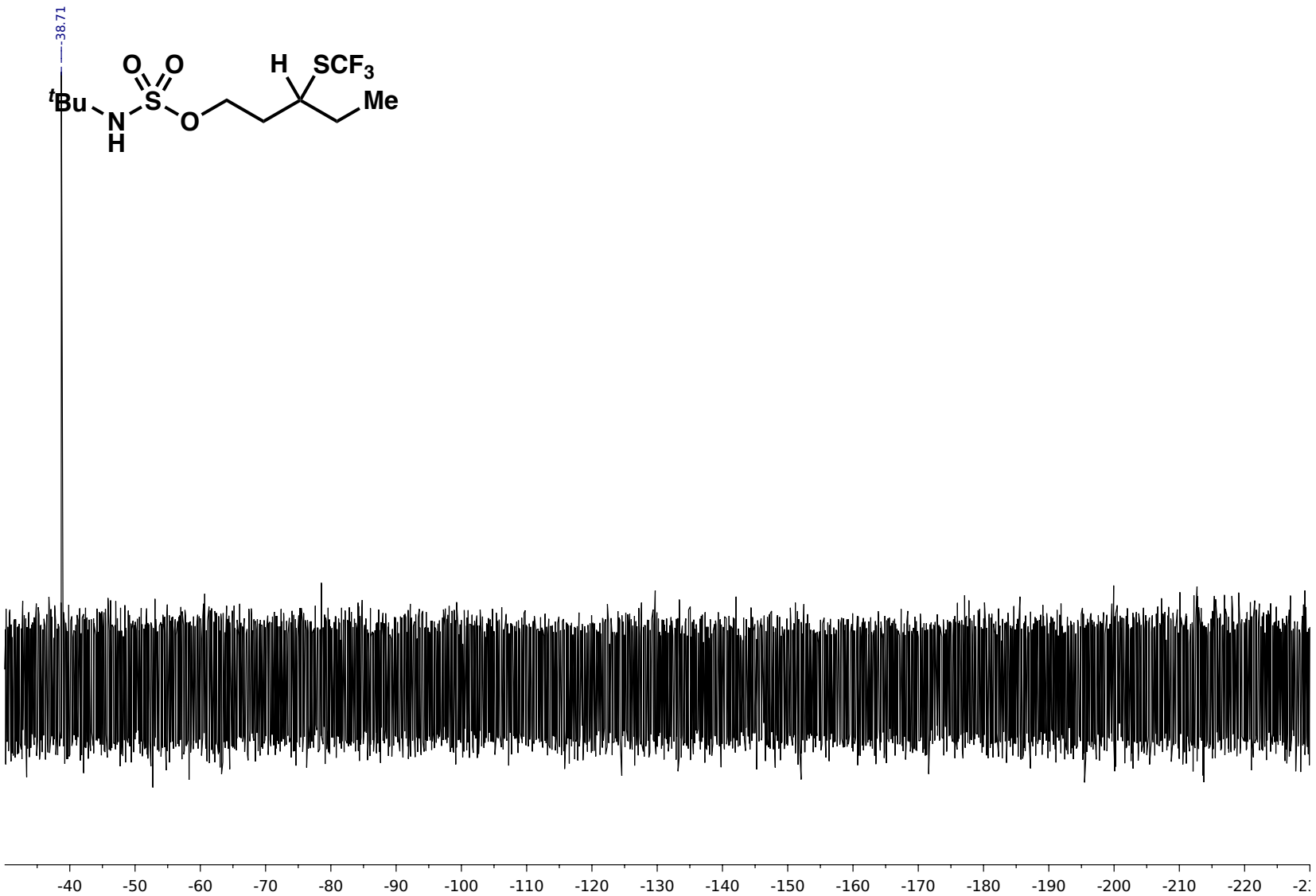
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-azido pentyl *tert*-butylsulfamate **(8)**



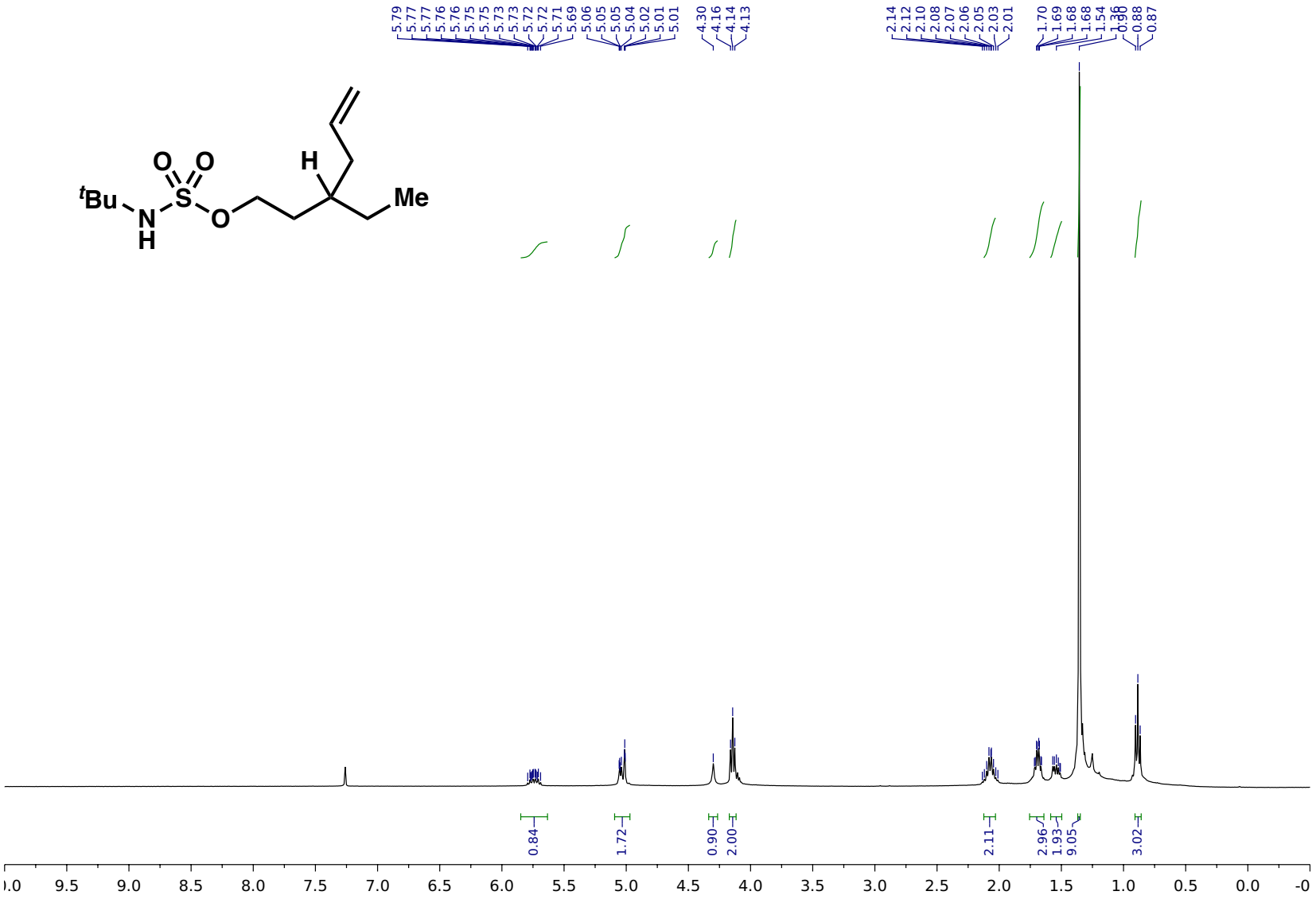
^{1}H NMR (400 MHz, $CDCl_3$) for 3-((trifluoromethyl)thio) pentyl *tert*-butylsulfamate **(9)**



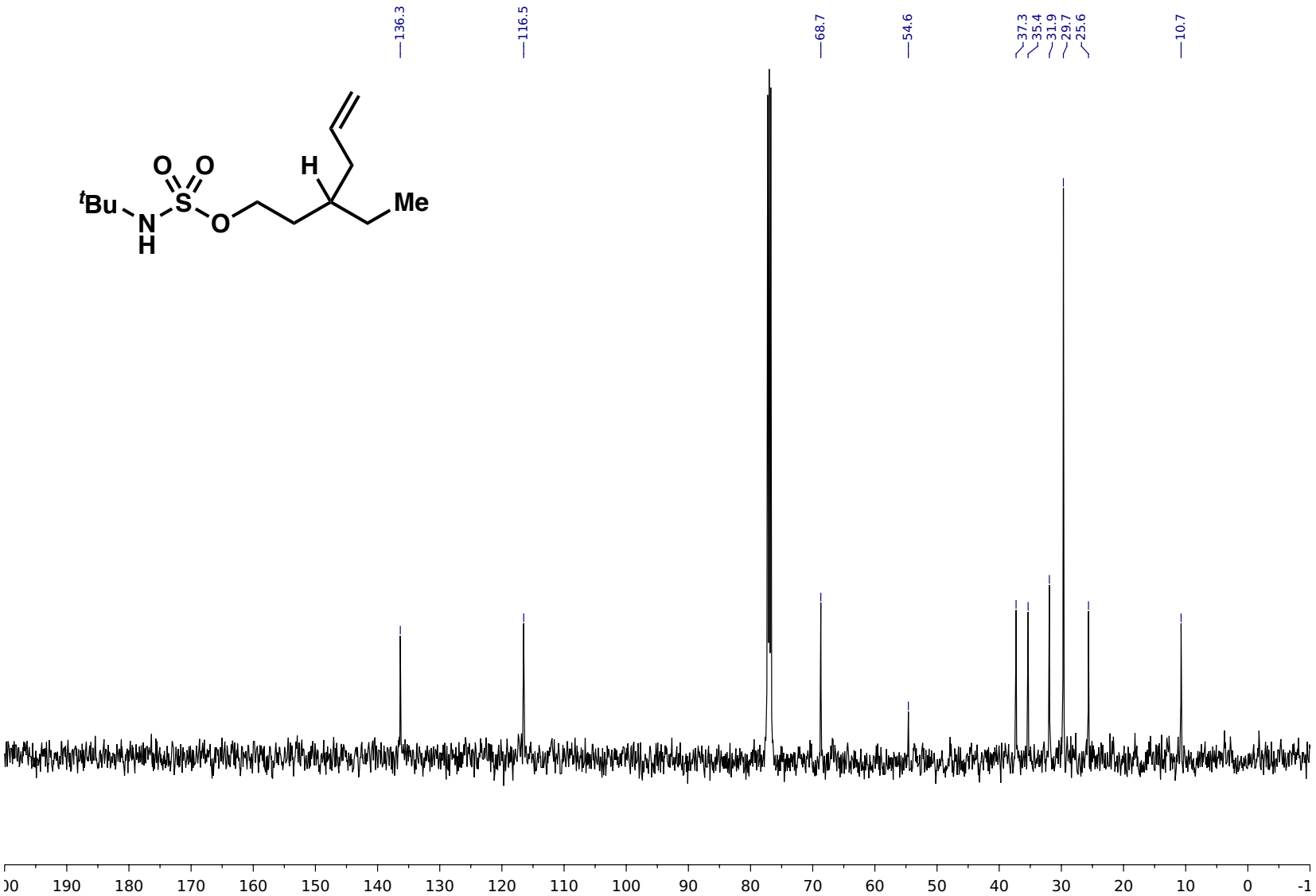
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-((trifluoromethyl)thio) pentyl *tert*-butylsulfamate **(9)**



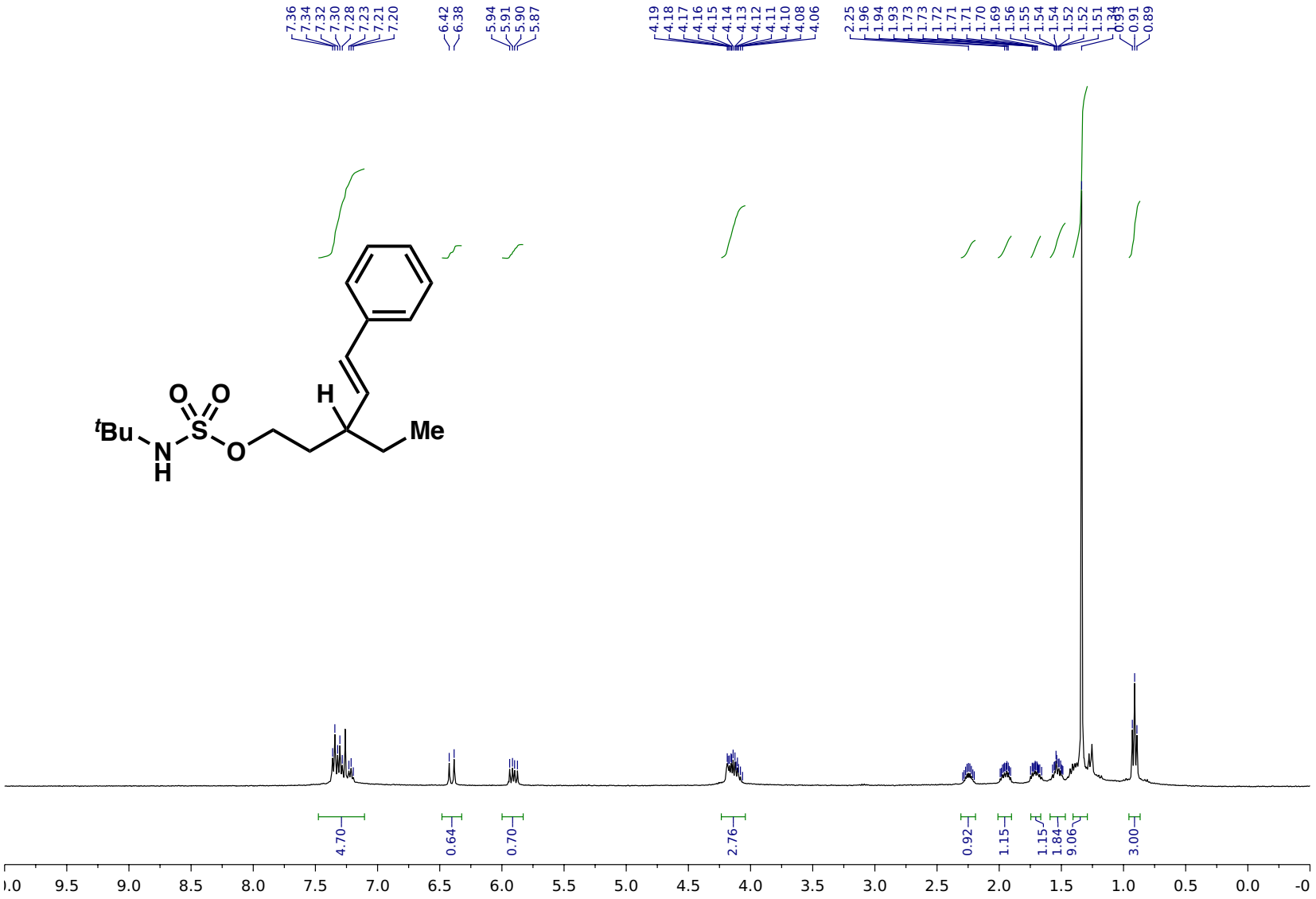
^{19}F NMR (376 MHz, $CDCl_3$) for 3-((trifluoromethyl)thio) pentyl *tert*-butylsulfamate **(9)**



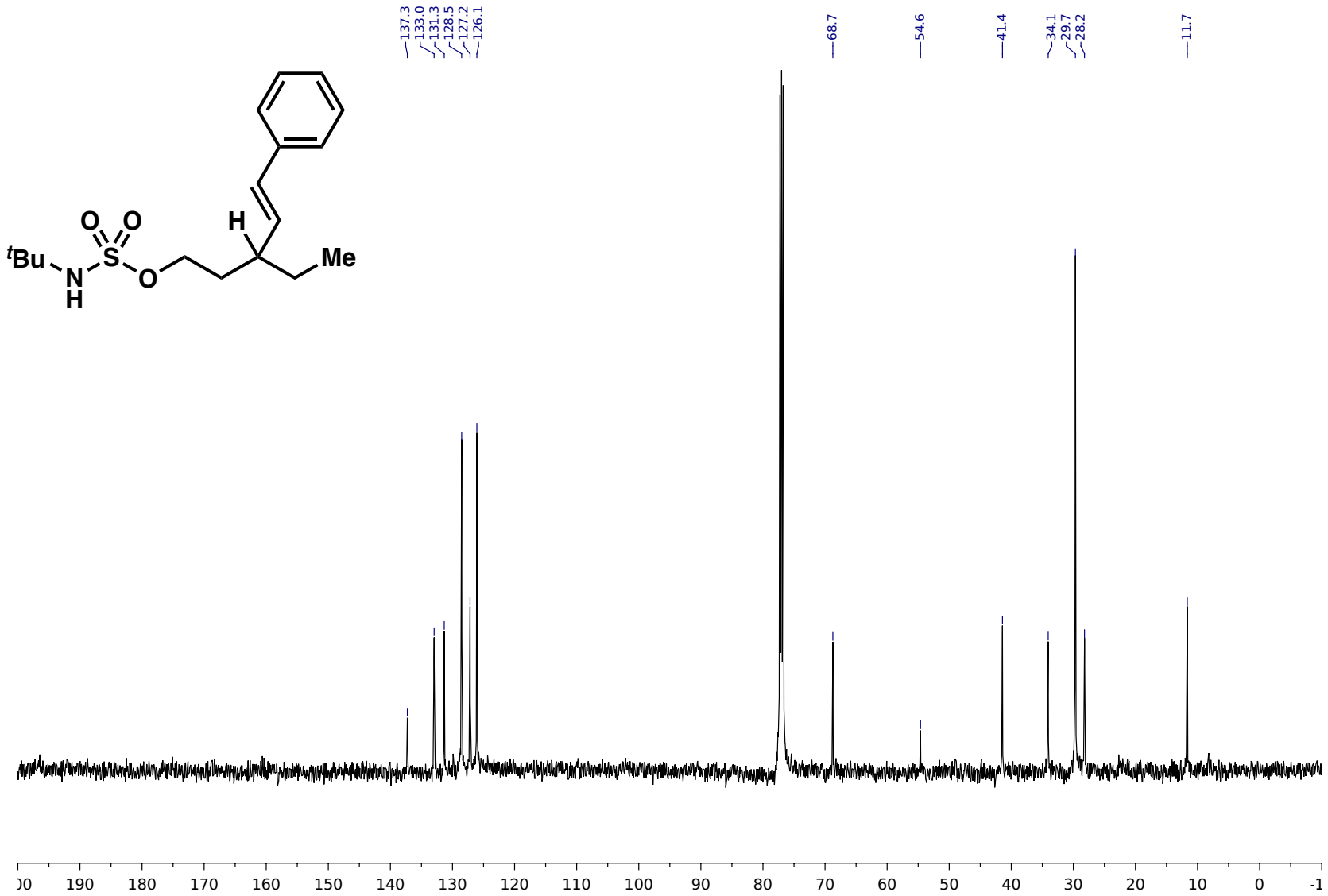
^{1}H NMR (400 MHz, $CDCl_3$) for 3-ethylhex-5-en-1-yl *tert*-butylsulfamate **(10)**



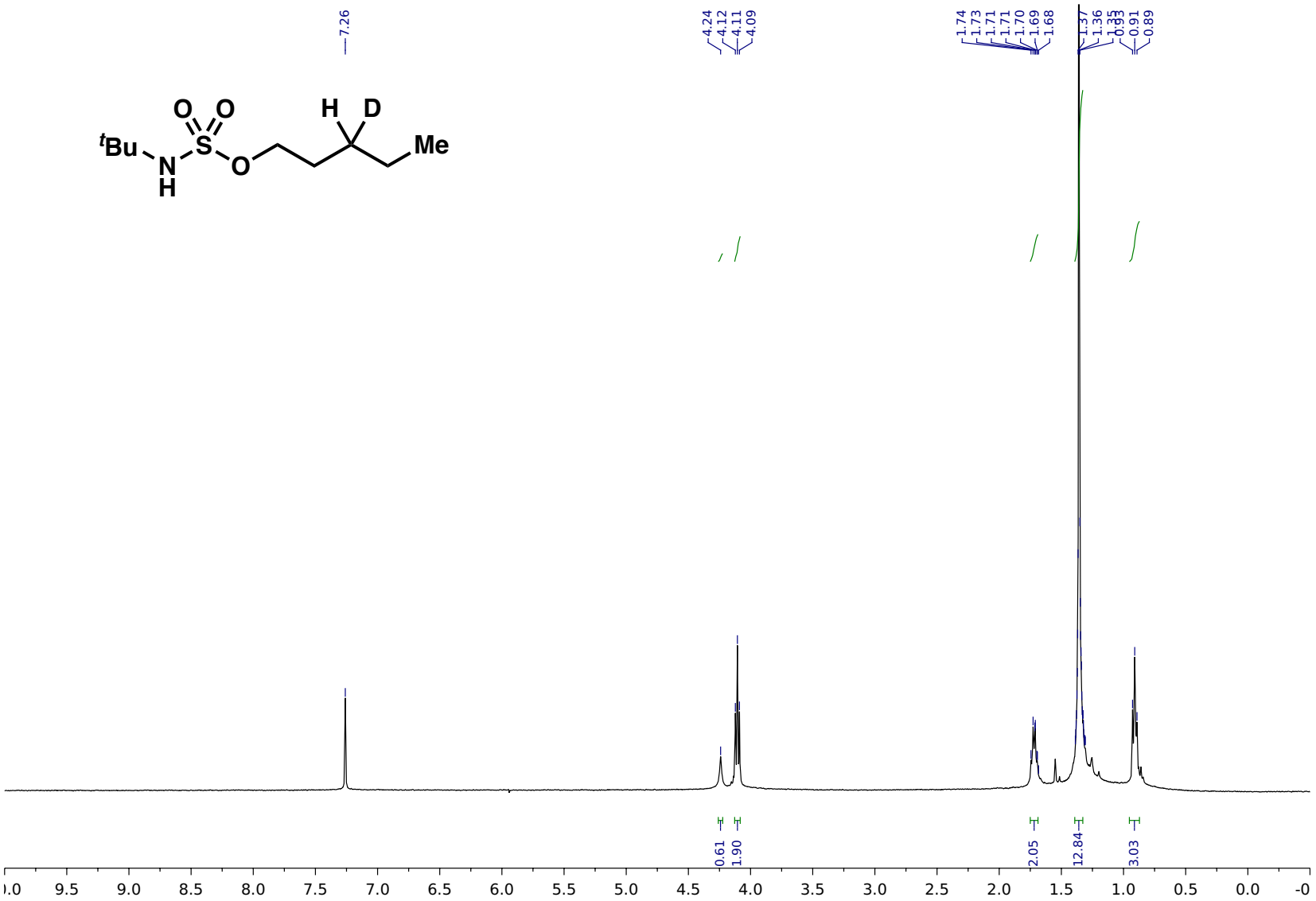
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-ethylhex-5-en-1-yl *tert*-butylsulfamate **(10)**



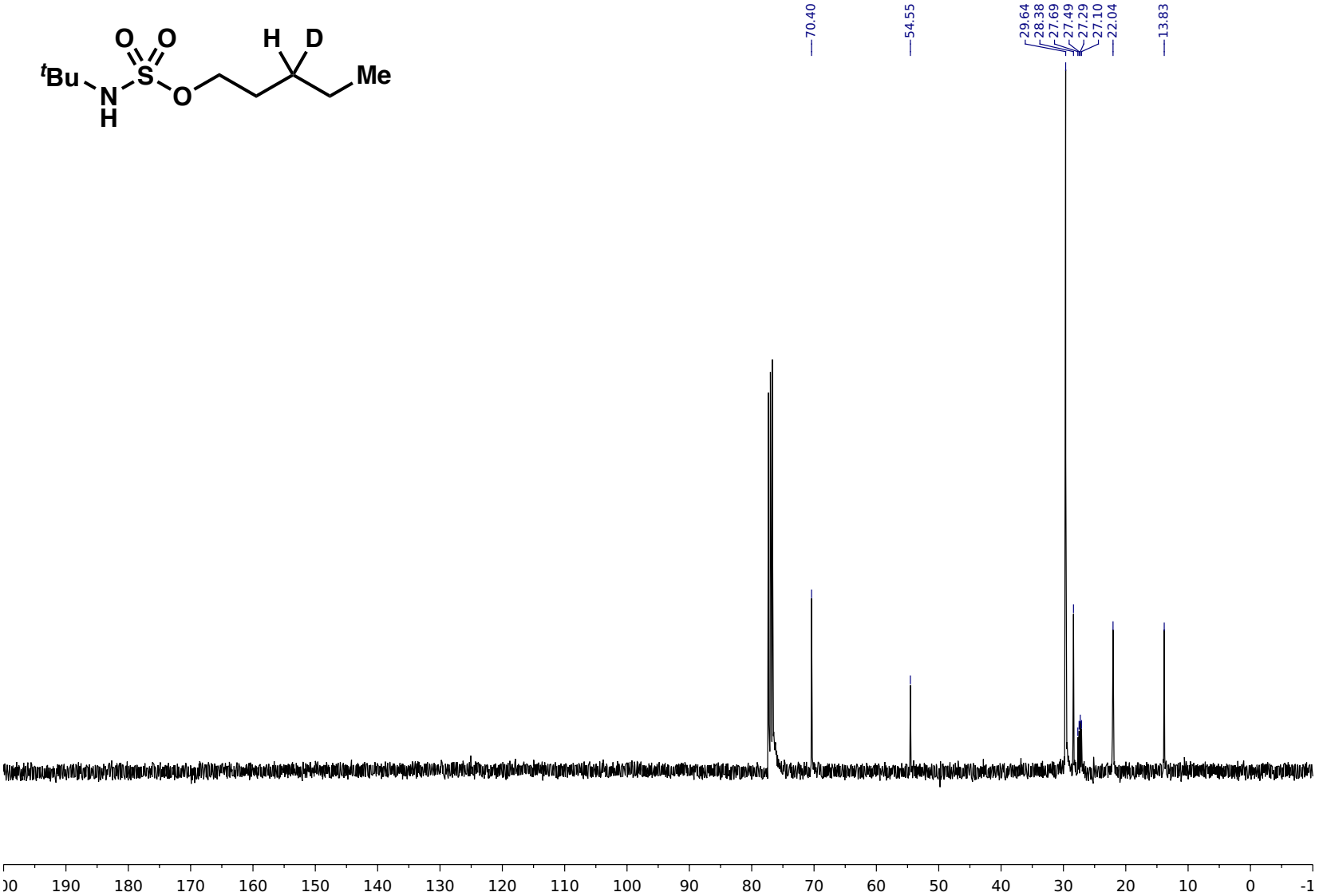
^{1}H NMR (400 MHz, $CDCl_3$) for 3-ethyl-5-phenylpent-4-en-1-yl *tert*-butylsulfamate **(11)**



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-ethyl-5-phenylpent-4-en-1-yl *tert*-butylsulfamate **(11)**



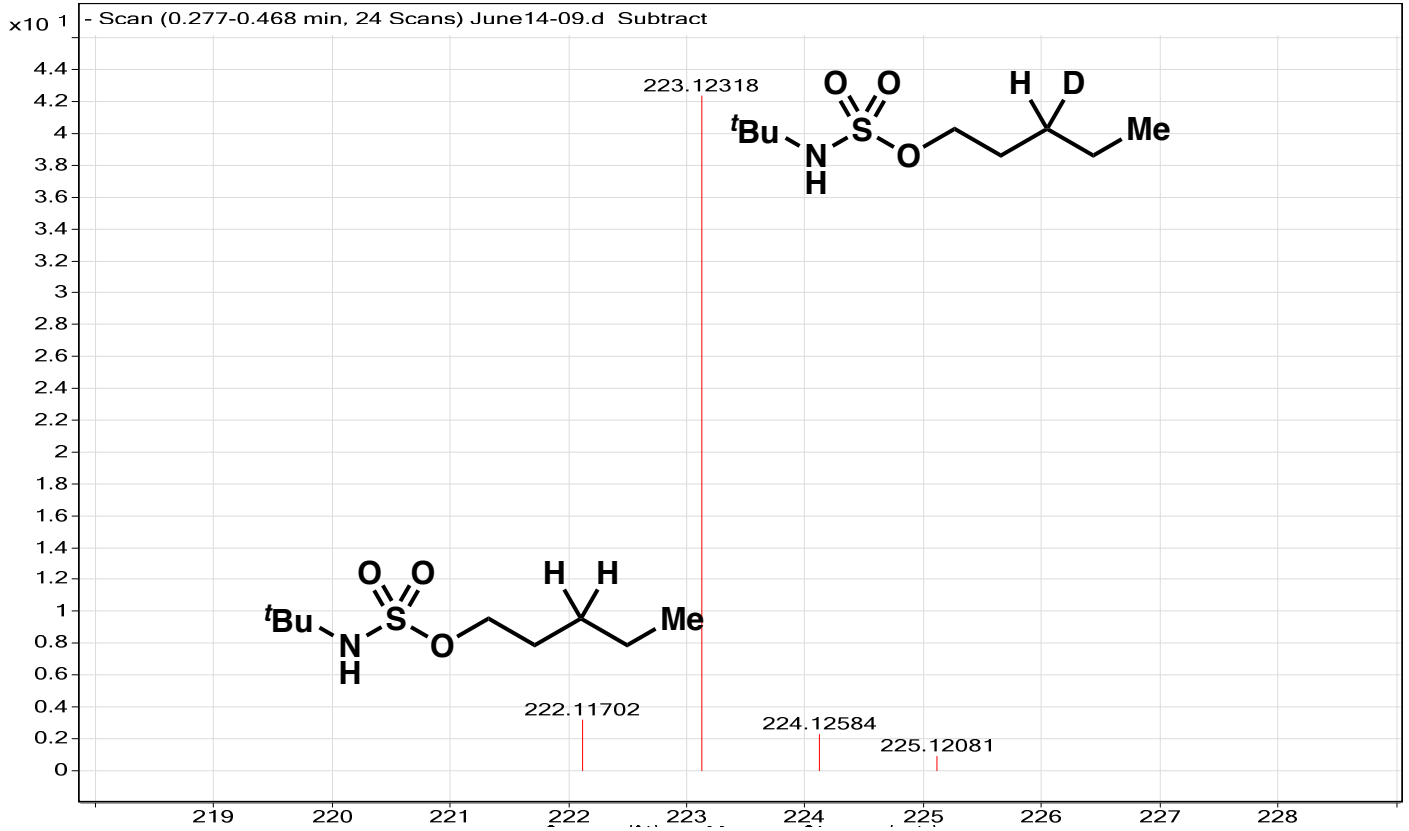
^{1}H NMR (400 MHz, $CDCl_3$) for 3-deuterio pentyl *tert*-butylsulfamate **(d-3a)**

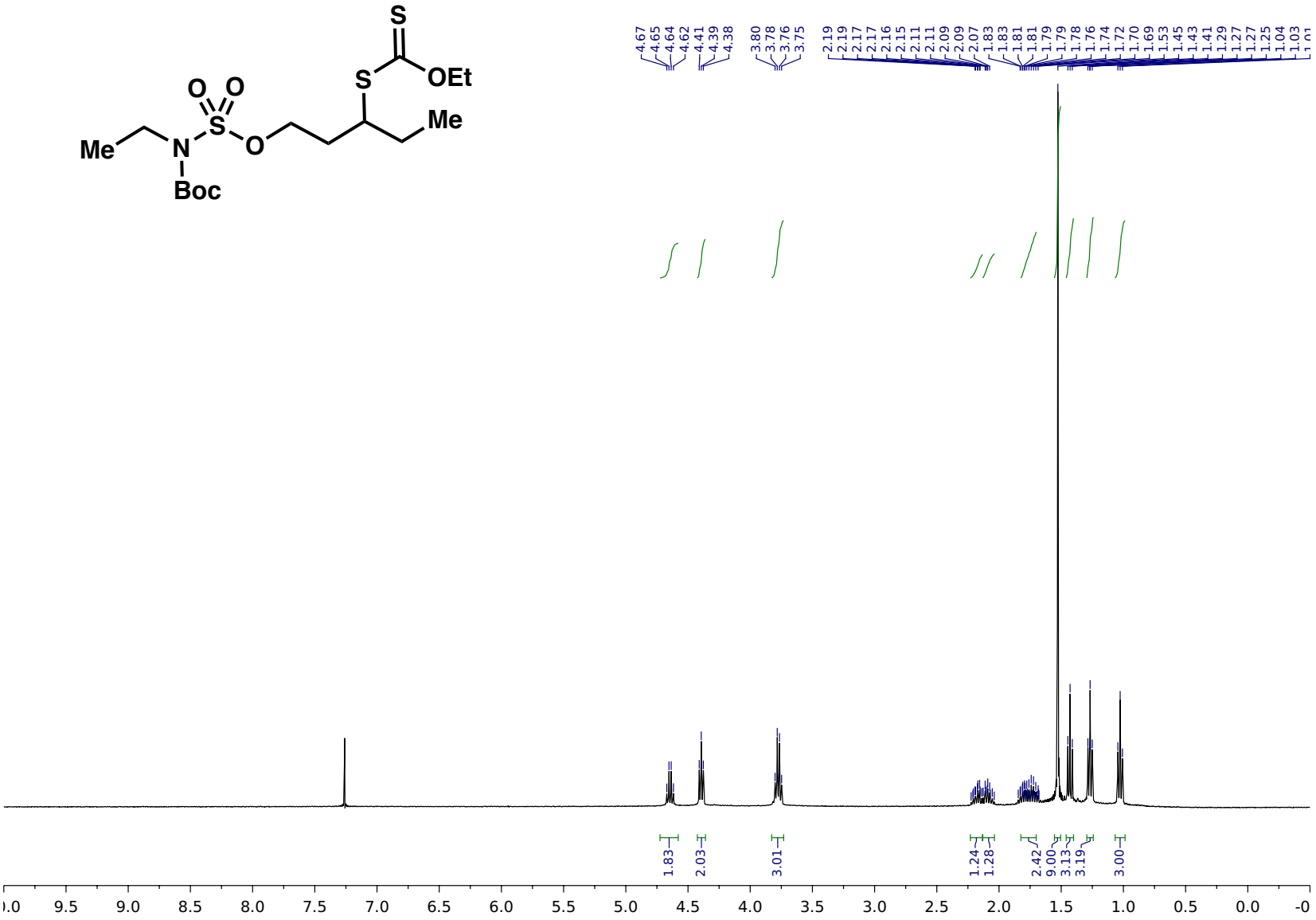


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) for 3-deuterio pentyl *tert*-butylsulfamate **(d-3a)**

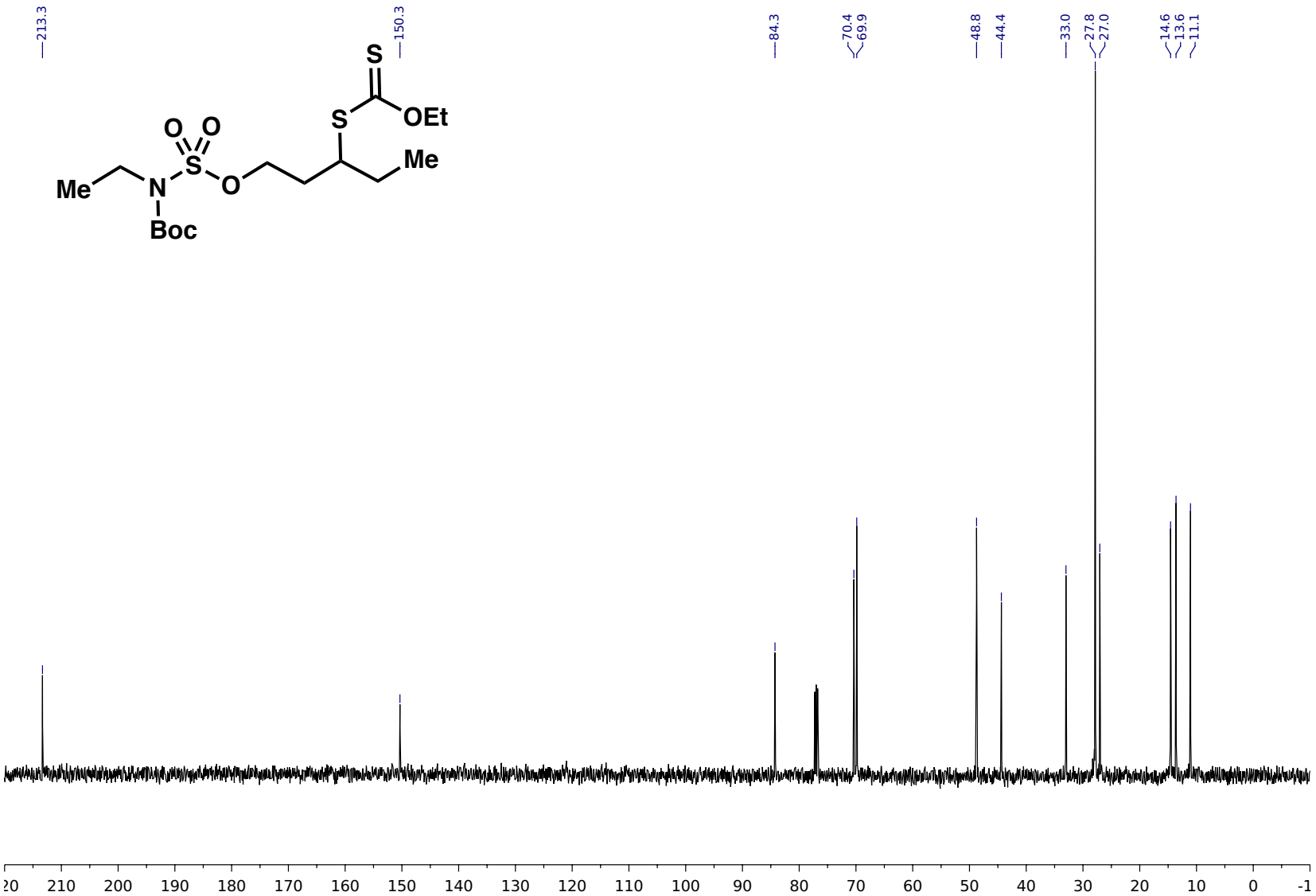
HRMS of **d-3a**

Sample Name	SKA-145b conc	**Position**	Vial 38	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	4	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	June14-09.d	**ACQ Method**	A1B1-iso50%-no col n	**Comment**	NoCol A1B1 iso 50:50 0.35 uL/min neg	**Acquired Time**	6/14/2018 12:15:59 PM

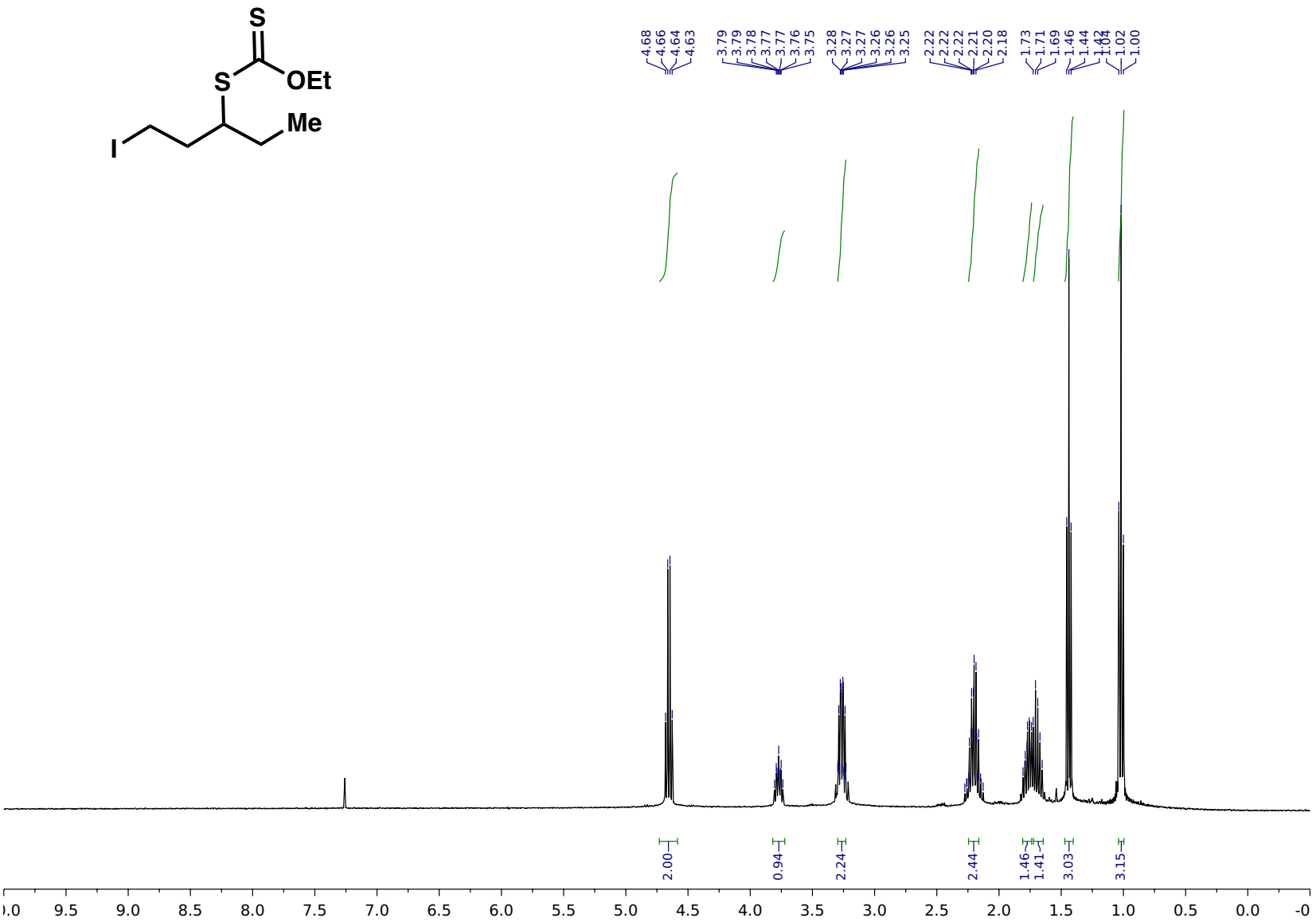




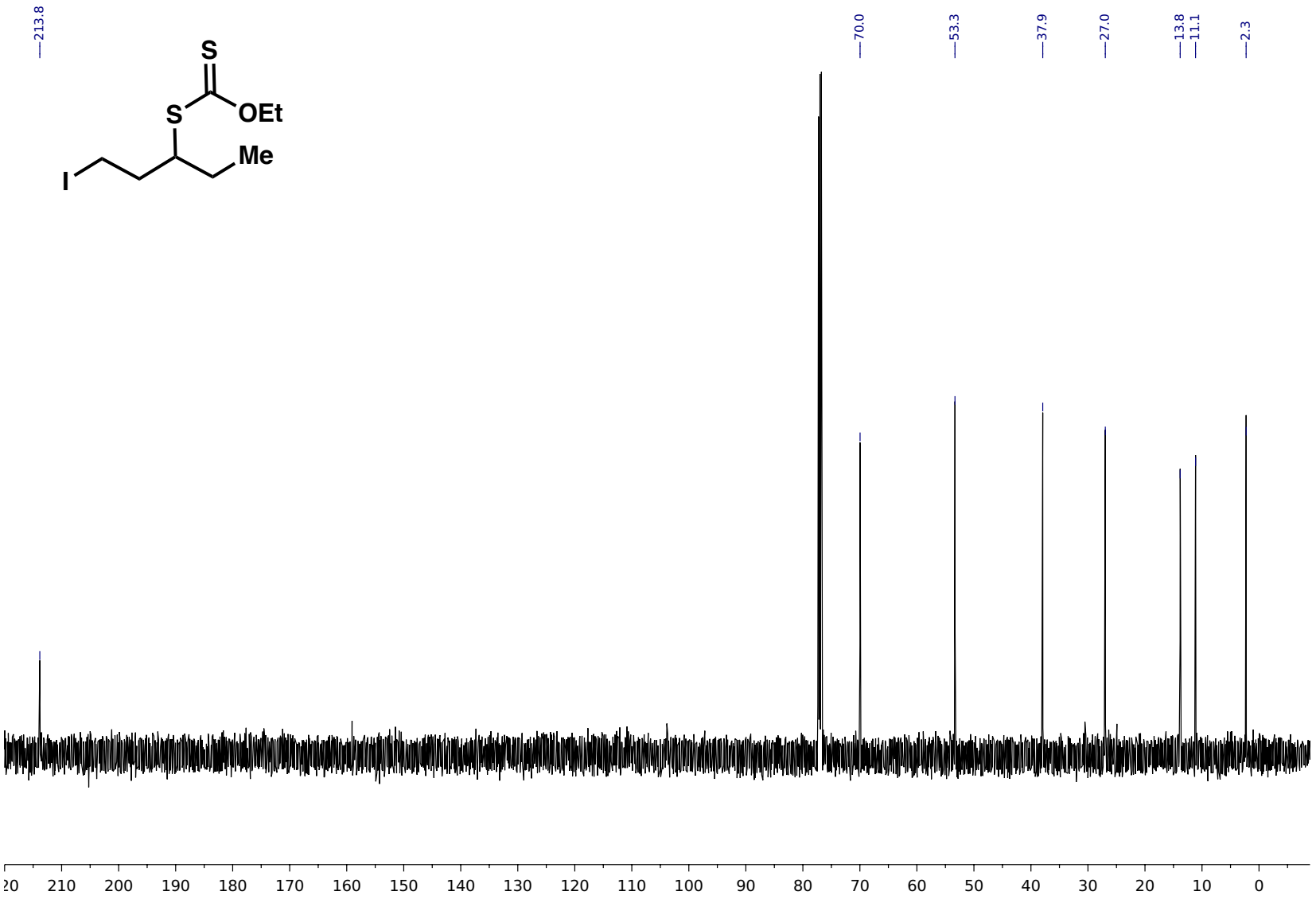
^{1}H NMR (400 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl (*tert*-butoxycarbonyl)(ethyl)sulfamate **(S5)**



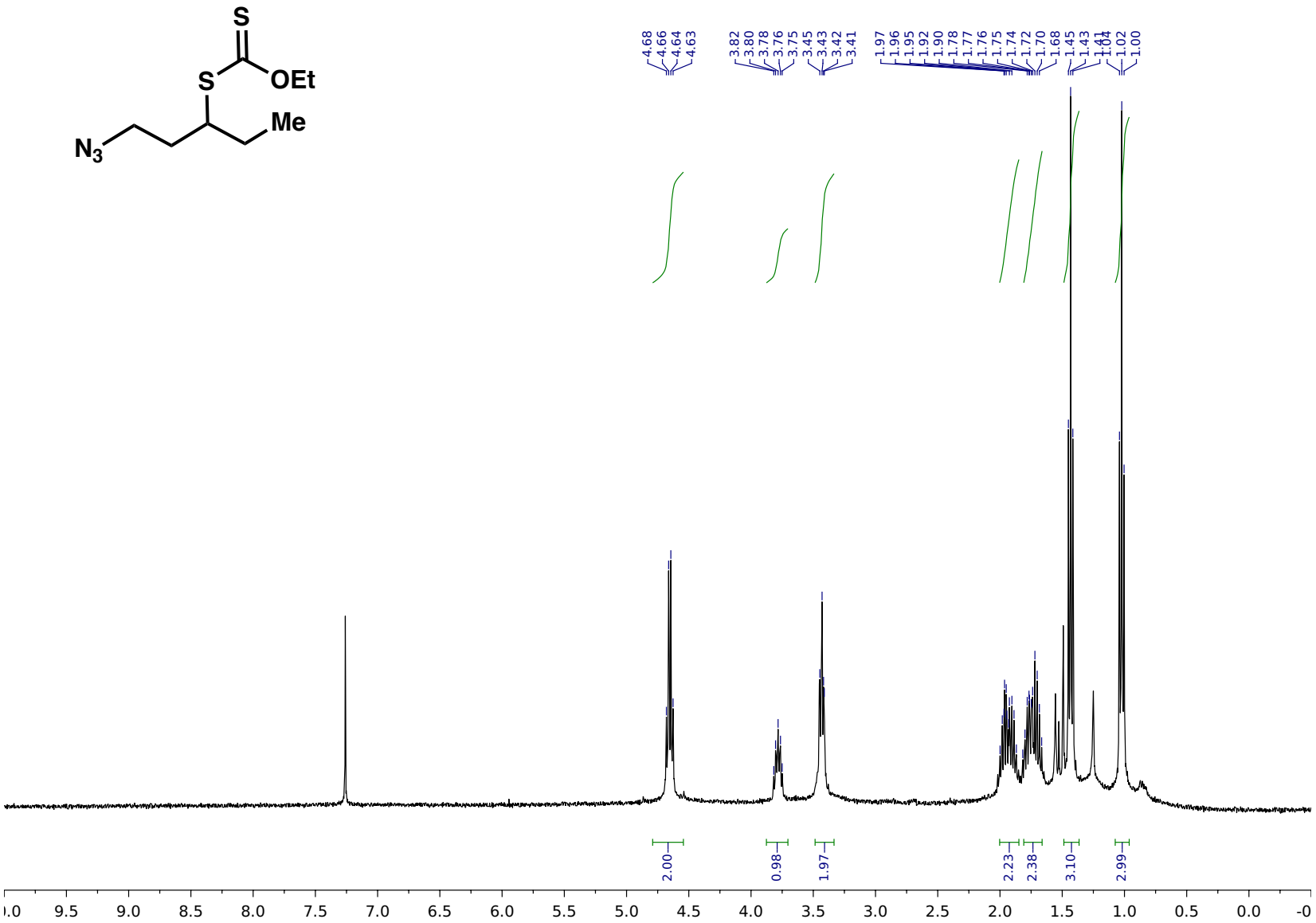
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl (*tert*-butoxycarbonyl)(ethyl)sulfamate **(S5)**



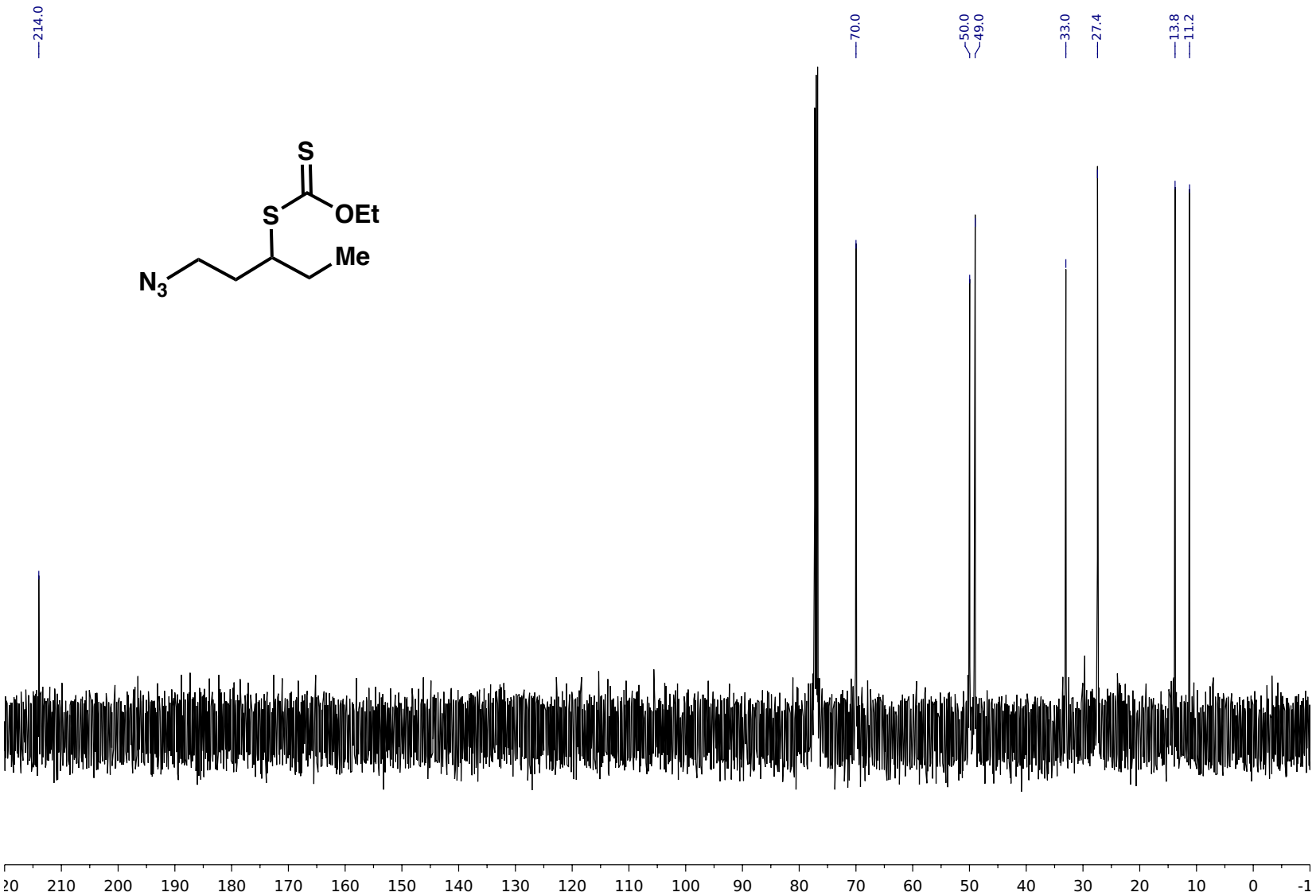
^{1}H NMR (400 MHz, $CDCl_3$) for *O*-ethyl (1-iodopentan-3-yl) carbonodithionate **(12)**



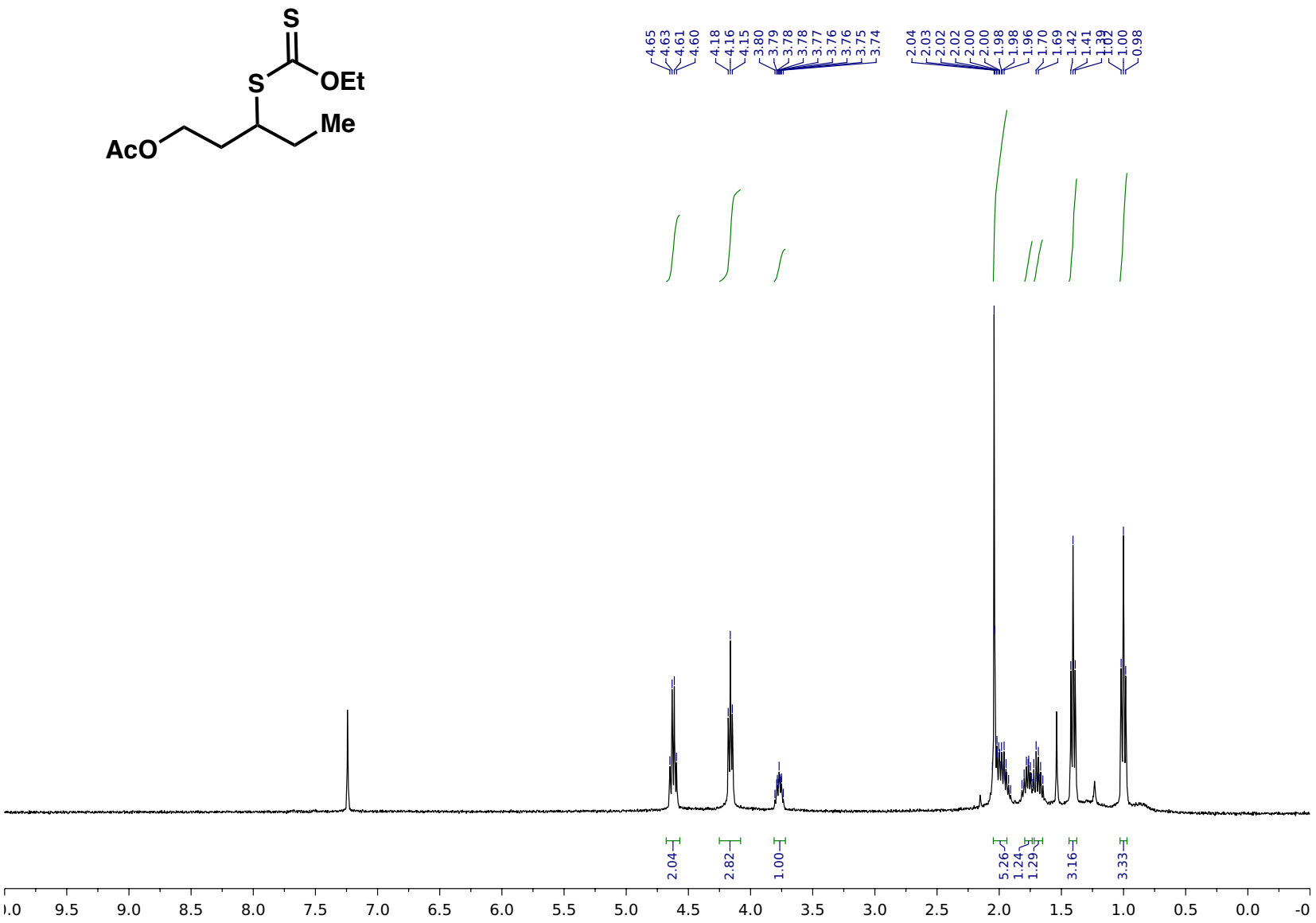
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for *O*-ethyl (1-iodopentan-3-yl) carbonodithionate **(12)**



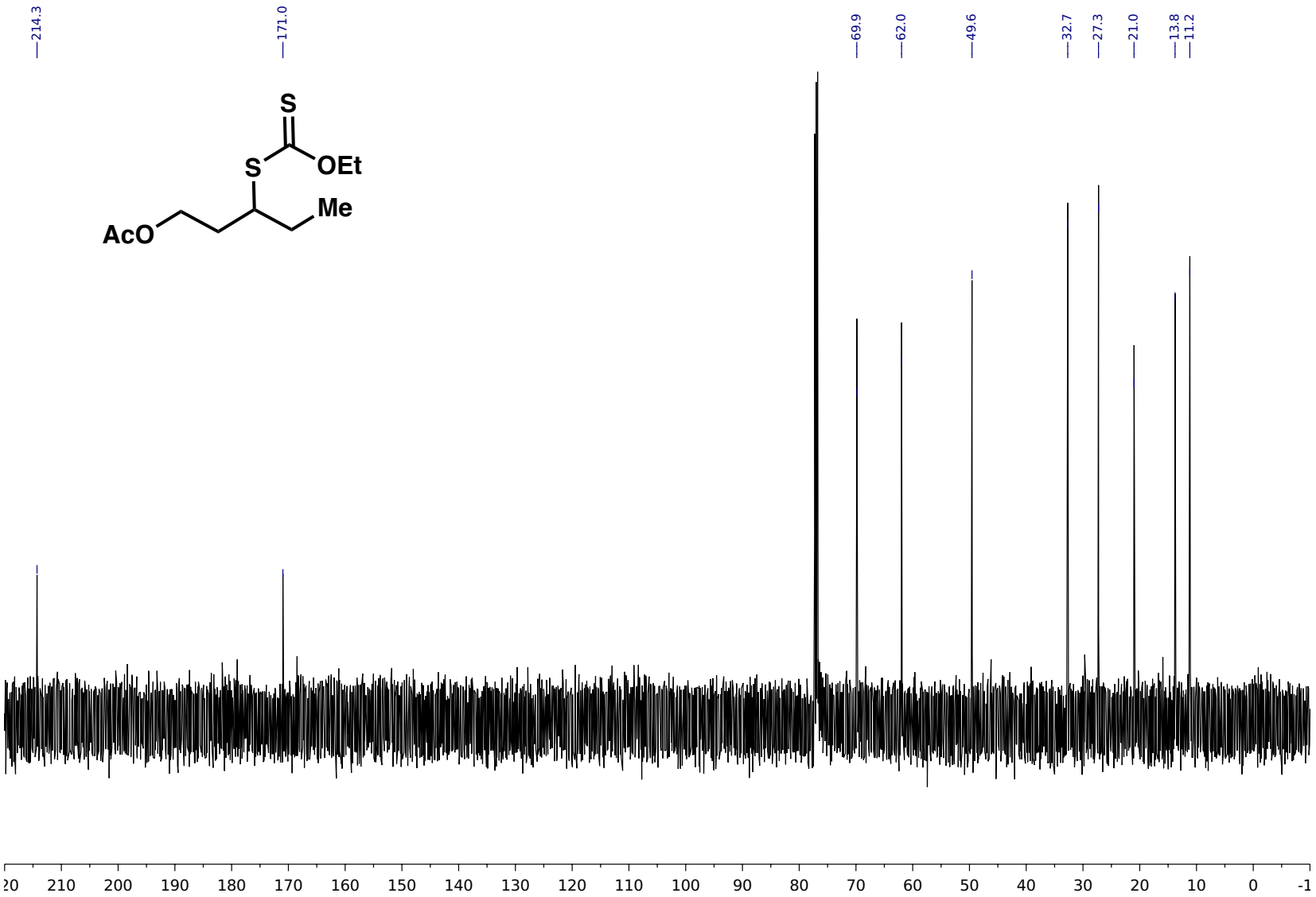
^{1}H NMR (400 MHz, $CDCl_3$) for (1-azidopentan-3-yl) *O*-ethyl carbondithioate **(13)**



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for (1-azidopentan-3-yl) *O*-ethyl carbondithioate **(13)**



^{1}H NMR (400 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl acetate **(14)**



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) for 3-((ethoxycarbonothioyl)thio)pentyl acetate **(14)**